Modeling of Noncatalytic Gas-Solid Reactions

This paper presents a critical review of the developments in the mathematical modeling of gas-solid noncatalytic reactions with particular emphasis on recent trends in the subject. A number of models proposed for analyzing this class of reactions have been reviewed with a fairly detailed discussion of the methods of incorporating structural changes which occur in the solid with the progress of reaction. The present status on the modeling of various types of complex gas-solid reactions is reviewed. Also the paper points out a number of areas in which future research may be needed. The review concludes with a critical discussion on the type of experimental data necessary for model verification and some comments on the choice of model for a given system.

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SCOPE

Noncatalytic gas-solid reactions are encountered in a variety of chemical process industries. The major applications are found in the fields of extractive metallurgy, control of gaseous pollutants, coal gasification processes, combustion of solid fuels, catalyst manufacture, etc. The mathematical modeling of these systems is important in order to interpret laboratory data on these systems and in design and scale-up. The problem is complex since in addition to the interplay of heat and mass transfer, other considerations are necessary to account for the transient nature of the problem and the effects of changes in solid properties with the course of reaction. Some of the major developments in this area have been reviewed in a book by Szekely et al. (1976) and in an edited monograph by Sohn and Wadsworth (1979). Since then considerable advances have taken place, and it is felt that there is a need for a comprehensive and critical review of the major recent developments in this area, and this review is written with this objective. Such a review also helps in evaluating some of the trends in research in this field.

CONCLUSIONS AND SIGNIFICANCE

In this review the various models which are commonly used to describe gas-solid noncatalytic reactions have been discussed. The three common models which have been in use are the sharp interface model, the volume reaction model, and the particle-pellet model. These models have been recently modified to take into account the effects of structural changes due to chemical reaction and sintering. Also new models which take into account the basic porous nature of the solid and the pore size distribution have been proposed. The review covers all these major developments. Further, in each case the model parameters and their physical significance have been clearly indicated.

Another important area of research is in the field of complex gas-solid noncatalytic reactions. A classification of the important reactions belonging to this class has been presented and the major developments in the modeling of these have been pointed out. The review also covers special characteristics of gasification and decomposition reactions and reactions showing significant nucleation effects. The information on the stability of noncatalytic gas-solid reactions is also breifly reviewed. Finally the review comments critically on the type of experimental data required for model evaluation and attempts a critical qualitative comparison of various models.

A general type of gas-solid noncatalytic reaction may be represented as

$$\nu_A A_{(g)} + \nu_B B_{(s)} \rightleftharpoons \nu_P P_{(g)} + \nu_C G_{(s)} \qquad \text{(i)}$$

in which a gas and a solid react to give gas and solid products. In some cases a gas and solid may yield only solid products ($\nu_P = 0$). Modeling of these two types of reactions is very similar and discussed in considerable detail in this paper. In some cases a solid reactant decomposes to yield gaseous and solid products ($\nu_A = 0$) and such reactions are known as decomposition reactions. Finally another important class of reactions is where only gaseous products are formed ($\nu_G = 0$) and such systems belong to the "gasification" reactions. Special features of modeling of decomposition and gasification reactions are also brought out in this review.

For modeling the general reactions represented by Eq. i, three types of models have been proposed: (i) in which the solid is assumed to be nonporous, the reaction occurring in a topochemical manner; (ii) where the solid reactant is assumed to be porous; and (iii) where the solid pellet is assumed to be composed of nonporous subunits known as particles or grains. These models are first discussed in the following sections.

SHARP INTERFACE MODEL

The sharp interface model is one of the earliest models used and is well described in standard textbooks on chemical reaction engineering. Hence we shall confine our attention here to the significant refinements which have been published recently. The model is mainly applicable to highly nonporous solid reactants and assumes that the reaction occurs at a sharp interface that divides the exhausted outer shell (ash layer) and the unreacted core of the solid. The model development for an isothermal first order reaction with equimolal counterdiffusion of reacting gases and product gases is straightforward and leads to an analytical relation for conversion-time behavior (for example, Wen, 1968; Sampath and Hughes, 1973; Szekely et al., 1976). The complexities that need to be accounted for are due to the effect of bulk flow (nonequimolal counterdiffusion), existence of pressure gradients in the pellet, nonisothermal effects and effects due to structural changes.

Detailed formulation accounting for the effects of bulk flow has been presented by a number of authors (for example, Beveridge and Goldie, 1968; Gower, 1971; Sohn and Sohn, 1980). The last authors present analytical solutions for a particular case when diffusion in the product layer is rate-controlling. The influence of pressure gradients has been examined by Deb Roy and Abraham (1974), and Turkdogan et al. (1973). These gradients are significant when Knudsen diffusion predominates in the pores of the product layer. Deb Roy and Abraham (1974) have given detailed numerical solutions to the pressure gradients which arise because of the Knudsen flow existing in the ash layer with small pores and due to the reactant gas having a diffusivity different from that of the product.

Many gas-solid reactions do not obey first-order kinetics and follow fractional order with respect to the gaseous reactant A. Examples are found in the reduction of Cr_2O_3 by H_2 (Chu and Rahmel, 1979), oxidation of ZnS (Cannon and Denbigh, 1957). As strong adsorption of A on the surface of the solid reactant B is often responsible for this behavior, such systems may equally well be represented by a Langmuir-Hinshelwood kinetics. For nonlinear systems, the conversion-time relations have to be obtained by numerical integration and the methods for doing this have been described by Sohn and Szekely (1972a) for power-law kinetics and by Ramachandran (1982a) for a Langmuir-Hinshelwood kinetics.

An interesting case of zero-order reactions has been reported by Simonsson (1979) for the reaction of NH_4F with $CaCO_3$ particles. The modeling of a zero-order reaction has also been presented by this author. For this case, the transition between kinetic and diffusion control is very sharp and the process is either entirely controlled by kinetics or by mass transfer. A combination of first- and zero-order kinetics has been proposed for the oxidation of coal by Kam et al. (1976). As the reaction was assumed to follow two distinct pathways, the rate of reaction consisted of two terms: one with first-order dependence on oxygen concentration and the other independent of oxygen. Some aspects of modeling of such systems have been discussed by these authors.

When the reaction is accompanied by large heat effects, nonisothermal models are required. An added complexity arises here due to the fact that the pseudosteady-state assumption which is generally used in the mass balance is not a good approximation for heat transfer (Beveridge and Goldie, 1968). Hence, a transient heat balance equation which includes the heat capacity of the pellet is needed. A simple model here is to assume that the entire solid is at a uniform temperature at a given time and the entire resistance to heat transfer lies in the gas film. This is a reasonable approximation in many cases and is generally valid when $h \ll k_e/R$. The validity of this assumption for gas-solid catalytic reaction has been demonstrated by Carberry (1961). For the more general case equations for predicting the complete transient temperature profile in the pellet have been derived by Luss and Amundson (1969). Solutions of this in conjunction with the equations for the rate of movement of the reaction interface provide a useful approach for obtaining both x-t and $T(r)$-t patterns of behavior of the pellet. A fairly general computer programme for this purpose which also incorporates the variation of physical properties with temperature has been developed by Prasannan et al. (1982).

The prediction of temperature profiles in the pellet may be the key problem in some situations. For example, in catalyst manufacture by reduction of metal salts or in the oxidation of coke from spent catalyst the temperature rise in the pellet has to be restricted below a permissible maximum in order to prevent catalyst deactivation. Shettigar and Hughes (1972) have developed models for the problem of coke regeneration. A related problem is encountered in ash agglomeration for reaction of carbon with oxygen and steam (Rehmat and Saxena, 1980). The ash gets agglomerated only if sufficiently high temperatures are reached within the particle. The theory developed by Rehmat and Saxena can be used to predict these conditions.

The structural changes due to chemical reaction generally lead to a change in the pellet size, and models to account for this have been developed by Shen and Smith (1963) for isothermal systems and by Rehmat and Saxena (1977) and Rehmat et al. (1978) for nonisothermal systems. A model to account for changes in the effective diffusivity of gas in the product layer (D_{eG}) with time due to the process of sintering has been discussed by Evans et al. (1973).

The concept of effectiveness factor commonly used for catalytic systems can be used to account for the diffusional effects in noncatalytic systems. Such an approach was first suggested by Ishida and Wen (1968). It may be noted here that the effectiveness factor for a noncatalytic reaction is a function of time unlike that for catalytic systems.

The sharp interface model has the advantage of mathematical simplicity although it should be used only for relatively nonporous solids. The major model parameters are the surface reaction rate constant k_s and the effective diffusivity of gas in the ash layer D_{eG}. The parameter D_{eG} should preferably be measured from independent experiments and compared with the value obtained from x-t data. This has been illustrated by Gokarn and Doraiswamy (1971, 1972) for the oxidation of zinc sulfide pellets.

VOLUME REACTION MODELS

Model Formulation

When the solid is porous, the gas can penetrate into the solid and the reaction may now be assumed to take place all over the volume of the pellet rather than at a sharp interface. The models which represent this situation are known as volume reaction models. The rate of reaction at the interior points would be of course generally lower than that at the surface due to diffusional gradients. The rate of reaction per unit volume of the pellet at a radial position r is represented in this model by the following equation:

$$r_A = k_v A^m B^n \tag{1}$$

where m and n are the order of reaction with respect to the gaseous species A and the solid reactant B respectively.

Based on this model the equations for mass and heat transfer within a spherical pellet can be represented as:

$$\nabla^2 a = \Omega \phi^2 \exp\left[\gamma\left(1 - \frac{1}{\theta}\right)\right] \tag{2}$$

$$\nabla^2 \theta + \beta \phi^2 \Omega \exp\left[\gamma\left(1 - \frac{1}{\theta}\right)\right] = N_2 \frac{d\theta}{d\tau} \tag{3}$$

$$\frac{db}{d\tau} = -\Omega \exp\left[\gamma\left(1 - \frac{1}{\theta}\right)\right] \tag{4}$$

where Ω is the local rate of reaction in terms of dimensionless concentrations and is defined as:

$$\Omega = a^m b^n \tag{5}$$

The other dimensionless parameters ϕ, β, γ and dimensionless time τ are defined in Table 1. (The stoichiometric coefficient ν_A is taken as unity here and in subsequent portions of the text without loss of

TABLE 1. DIMENSIONLESS PARAMETERS IN VOLUME REACTION MODELS

Parameter	Notation	Definition
1. Thiele Modulus	ϕ	$\|R^2k_v(T_o)A_g^{m-1}B_o^n/D_e\|^{1/2}$
2. Biot Number for Mass Transfer	Bi_M	k_gR/D_e
3. Biot Number for Heat Transfer	Bi_H	hR/D_e
4. Thermicity factor	β	$(-\Delta \mathrm{H})D_eA_g/(k_eT_o)$
5. Arrhenius Number	γ	$E/(R_gT_o)$
6. Heat Accumulation Parameters	N_2	$\nu_B\rho_Pc_pR^2k_v(T_o)A_g^mB_o^{n-1}/k_e$
7. Dimensionless Time	τ	$\nu_Bk_v(T_o)A_g^mB_o^{n-1}t$

generality.) For isothermal systems, only the mass balance equations (Eqs. 2 and 4) need to be considered. In the formulations of the heat balance equation (Eq. 3) the transient terms have been included as these terms are often important in determining the temperature profile and conversion in the pellet. The latter quantity is defined as:

$$x(\tau) = 3\int_0^1 y^2 b\, dy \tag{6}$$

where y is the dimensionless distance r/R in the pellet.

The boundary and initial conditions are standard and are given as:

$$\text{At } y = 1, \frac{da}{dy} = \mathrm{Bi}_M(1 - a) \tag{7}$$

$$\frac{d\theta}{dy} = \mathrm{Bi}_H(1 - \theta) \tag{8}$$

$$\text{At } y = 0, \quad \frac{da}{dy} = \frac{d\theta}{dy} = 0 \tag{9}$$

and

$$\text{at } \tau = 0, \quad \theta = 1, \quad b = 1 \tag{10}$$

It is seen from the above formulation that for the simple case of isothermal systems the volume reaction model has four parameters: k_v, D_e (effective diffusivity of gas in porous solid B), m and n.

Discussion of Some Specific Cases

The case of (1,0) order reaction ($m = 1, n = 0$) has been analyzed by Ausman and Watson (1962) and Ishida and Wen (1968). These authors divided the total reaction time into two periods: (a) constant rate period, and (b) falling rate period. The necessity for considering two such separate periods arises because the concentration of B can actually become zero at the surface after the elapse of a particular time, whenever the reaction order, n, is less than unity. (This time is equal to $B_o^{1-n}/[(1-n)k_vA_g^m]$ when $\mathrm{Bi}_M \rightarrow \infty$ for an isothermal system.) After this time, a product layer forms near the surface through which gas A has to diffuse without reacting before it can reach the reactant B. The pellet then comprises two zones: (a) product layer $\lambda < y < 1$, and (b) a reaction zone $0 < y < \lambda$ (Figure 1). The model Eqs. 2, 3 and 4 are valid only for the reaction zone. In the region $\lambda < y < 1$ the quantities Ω and b are zero and model has to be solved as a set of coupled differential equations. Also the problem becomes one of the moving boundary value type as the position λ moves inward into the pellet with time. When the rate of reaction is fairly rapid ($\phi > 5$), the concentration of A drops very sharply in the reaction zone which may now be further divided into two zones: (b-1) reaction zone, and (b-2) core of completely unreacted B. This then leads to the three zone model proposed by Bowen and Cheng (1969), Tudose (1970) and Mantri et al. (1976). These models are also referred to as finite reaction zone models. Mathematically they are very similar to the two zone model proposed by Ishida and Wen (1968). The case of (1,1) and (1,0.5) order reaction ($m = 1$, $n = 1$ and 0.5) has been analyzed by Dudukovic and Lamba (1978a). For (1,1) order case there is no need to consider the presence of a completely reacted product layer because mathematically for a first order reaction ($n = 1$) the concentration of B at the surface can become zero only at $\tau = \infty$.

The case of $m = 0$, $n = 1$ has also been analyzed in detail by Dudukovic and Lamba (1978b). The model is likely to be applicable when the species A is strongly adsorbed on the solid so as to make the reaction zero order in A. However it may be worth noting here that such zero order behaviour is only an approximate representation of the system and the true kinetics may be a Langmuir Hinshelwood model with a large value of the equilibrium constant. Analytical solutions for x-τ behaviour for (0,1) case have been derived by Dudukovic and Lamba (1978b). A related problem of considerable theoretical interest occurs when the reaction is zero order with respect to both gas and solid ($m = 0$, $n = 0$). This has been analyzed in a recent paper by Ramachandran and Doraiswamy (1982). Here as both A and B can be completely consumed by reaction the pellet shows a "jumping reaction zone" behavior.

Model Solution Techniques

It is appropriate here to discuss some of the recent developments in the solution of the model equations to obtain the conversion-time behavior of the pellet. For isothermal reactions which are first order with respect to the gas a special technique has been developed by Del Borghi et al. (1976) and Dudukovic and Lamba (1978a) based on the concept of cumulative concentration. This variable is defined as:

$$C_m = \int_0^\tau a\, d\tau \tag{11}$$

Using this transformation Eq. 2 reduces to the following form for isothermal systems with $m = 1$

$$\nabla^2 C_m = \phi^2 F(C_m) \tag{12}$$

where

$$F(C_m) = 1 - [1 - (1-n)C_m]^{1/(1-n)} \quad \text{for } n < 1 \tag{13}$$

$$= 1 - \exp(-C_m) \quad \text{for } n = 1 \tag{14}$$

Equation 12 is easier to solve for C_m than the original coupled equations. The required boundary conditions are: (1) the condition of symmetry for C_m at the center, and (2) C_m = time elapsed (τ) at the surface for the case of no significant external transport resistance. The conversion in the solid is related to C_m by the following equation:

$$x = \frac{(1 + S_F)}{\phi^2}\left(\frac{dC_m}{dy}\right)_{y=1} \tag{15}$$

where S_F = shape factor of the pellet.

It may be noted here that Eq. 12 has the same form as that for a catalytic reaction with a nonlinear rate law. Hence various techniques available for the solution of such problems can be used here and approximate analytical solutions can be derived for a number of cases using, for example, a single collocation point approximation (Ramachandran and Kulkarni, 1980) or the asymptotic property of Eq. 12 (Ramachandran, 1982b). These approximate solutions are fairly close to the numerical solutions and hence are useful in estimating the model parameters since they avoid repeated numerical solution of the model for each set of assumed parameter values.

Approximate analytical solutions can also be derived by methods suggested by Sohn and Szekely (1972b) and Sohn (1978) or by using average solid concentration in the pellet (Wen and Wu, 1976). Other recent studies on model solution techniques are as follows: use of orthogonal collocation on the original set of equations (Boersma et al., 1980), collocation on the transient problem, that is, without using pseudosteady state hypothesis (King and Jones, 1979) and use of invariant imbedding methods (Bellman et al., 1977).

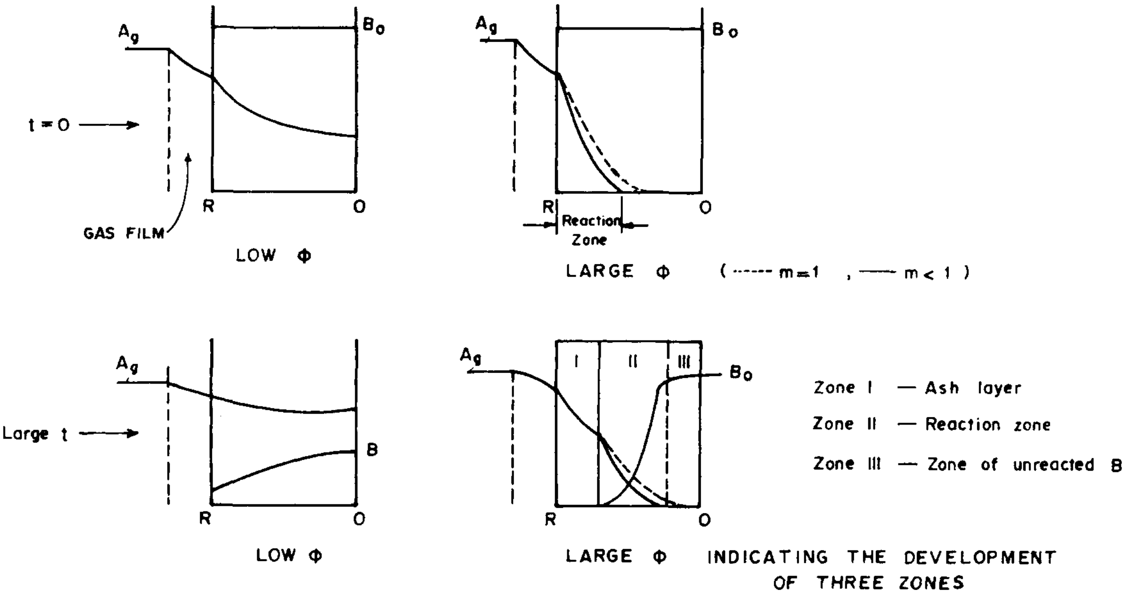

Figure 1. Concentration profiles for the homogeneous model for various Thiele modulus.

PARTICLE-PELLET OR GRAIN MODEL

In this model the solid pellet is visualized as consisting of a number of small particles or grains. Surrounding these grains are macropores through which the gas has to diffuse to reach the various grains. The reaction occurs at the surface of each grain according to the sharp interface model. A product layer will form with time in the outer regions of each grain and these will in turn offer some resistance to diffusion. A detailed analysis of this problem has been presented by Calvelo and Smith (1970) and Szekely and Evans (1971a, b, c). The rate of reaction per unit volume of the pellet on the basis of the grain model assuming spherical grains is:

$$r_A = \frac{3(1-\epsilon)\dfrac{k_s}{r_{Go}}\left(\dfrac{r_{Gi}}{r_{Go}}\right)^2 A}{1 + \dfrac{r_{Gi}k_s}{D_{eC}}\left(1 - \dfrac{r_{Gi}}{r_{Go}}\right)} \tag{16}$$

where

ϵ = porosity of the pellet
r_{Gi} = position of the reaction interface within the grain at a given time

and

r_{Go} = initial radius of the grain

The model equations for the particle-pellet model are then as follows:

$$\nabla^2 a = \phi_1^2 (r^*)^2 \Omega_1 \tag{17}$$

$$\nabla^2 \theta + \beta \phi_1^2 (r^*)^2 \Omega_1 = N_3 \frac{d\theta}{d\tau_1} \tag{18}$$

and

$$\frac{dr^*}{d\tau_1} = -\Omega_1 \tag{19}$$

where Ω_1 is defined as

$$\Omega_1 = \frac{a \exp\left[\gamma\left(1 - \dfrac{1}{\theta}\right)\right]}{1 + \dfrac{r^*}{\mathrm{Bi}_p}(1 - r^*)\exp\left[\gamma\left(1 - \dfrac{1}{\theta}\right)\right]} \tag{20}$$

The dimensionless parameters ϕ_1, τ_1 and Bi_p are defined in Table 2. In these equations, r^* corresponds to the reduced quantity r_{Gi}/r_{Go} at a position y in the pellet. The grain model has five parameters k_s, D_e, D_{eG}, r_{Go} and grain shape. Detailed numerical solutions for the isothermal case have been published by Calvelo and Smith (1970) and Sohn and Szekely (1972b, 1974). An approximate analytical solution for isothermal case has been proposed by Evans and Ranade (1980), Sohn and Szekely (1972b, 1974) and Ramachandran (1982b). The formulation of the problem as above is for a spherical grain. A general formulation which assumes various grain shapes such as spheres, long cylinders and slabs has been presented by Sohn and Szekely (1972b, 1974). The grain shape factor may either have a physical basis (as when pellets are formed by compaction) or it could be an empirical model parameter. There is a close analogy between the grain shape factor and the order of reaction with respect to solid in the volume reaction model for the situation when $D_{eG} \rightarrow \infty$. The values of n of 0, 0.5 and 0.67 correspond to grain shapes of flat plate, cylinder and sphere respectively.

For nonisothermal systems, numerical solutions have been obtained by Calvelo and Smith (1970) based on pseudo-steady state approximation ($N_3 = 0$ in Eq. 18). A complete transient problem for this case has been solved by Sampath et al. (1975). The transient model is necessary for predicting the temperature profiles in the pellet. A comparison of the temperature profiles obtained by the pseudosteady-state model and the transient model was done by Sampath et al. (1975). In the pseudosteady-state model the maximum temperature is attained at $\tau = 0$ while in the transient model it is attained after the lapse of a certain length of time. Another interesting result is that the pseudosteady-state model predicts that the maximum temperature is always attained in the center of the pellet. The transient model predicts that the maximum tempera-

TABLE 2. DIMENSIONLESS PARAMETERS IN PARTICLE PELLET MODEL WITH CONSTANT PARTICLE SIZE

Parameter	Notation	Definition
1. Thiele Modulus	ϕ_1	$\dfrac{3(1-\epsilon_o)k_s(T_o)R^2}{r_{Go}D_e}$
2. Particle Biot Number	Bi_p	$D_{eG}\,\lvert r_{Go}k_s(T_o)\rvert$
3. Heat Accumulation Parameter	N_3	$\nu_B R^2 M_B c_p k_s(T_o) A_g/(k_e r_{Go})$
4. Dimensionless Time	τ_1	$\nu_B t M_B A_g k_s(T_o)/(\rho_B r_{Go})$
5. Additional Parameters, Bi_M, Bi_H, β and γ; the definitions of these Same as in Table 1.		

TABLE 3. MODELS TO ACCOUNT FOR STRUCTURAL CHANGES DUE TO REACTION

Model Name/Type	References
1. Modified Volume Reaction Model	Wen (1968); Ishida and Wen (1968); Calvelo and Cunningham (1970); Gidaspow (1972)
2. Modified Particle-Pellet Model	Hartman and Coughlin (1974, 1976); Ramachandran and Smith (1977b); Georgakis et al. (1979); Ranade and Evans (1980); Ranade and Harrison (1981); Garza-Garza and Dudukovic (1981)
3. Single-Pore Models	Petersen (1957); Szekely and Evans (1970); Ramachandran and Smith (1977a); Chrostowski and Georgakis (1978); Ulrichson and Mahoney (1980); Lee (1980)
4. Distributed Pore-Size Models	Hashimoto and Silveston (1973a, 1973b); Simons and Rawlins (1980); Bhatia and Perlmutter (1980, 1981a, 1981b); Gavalas (1980); Christman and Edgar (1980)

ture occurs initially in a region close to the surface of the pellet which then moves towards the center as time progresses.

The grain model is particularly useful for the case where the pellet is formed by compaction of particles of very fine size. The grain size has a clear physical meaning for this case. When the pellets are not formed in this manner the radius for a spherical grain may be approximated as $3/(S_g \rho_p)$. The grain model has been applied to a number of systems such as the reduction of NiO (Szekely and Evans, 1971b; Szekely and Lin, 1976; Evans et al., 1976), and the hydrofluorination of UO_2 (Costa and Smith, 1971).

In a recent study, Gibson and Harrison (1980) have applied this model to the reaction of H_2S with ZnO. In this study all the model parameters were either determined or predicted independently. (For example, k_s was obtained from the rate data obtained with finely divided powders; the effective diffusivity was predicted from the random pore model of Wakao and Smith, 1962.) The only parameter which could not be obtained independently was D_{eG}. This was obtained by comparison of the rate data with the model predictions. The x-τ predictions of the grain model were in close agreement with the theory except in the low temperature range (600°C) where the reaction ceased before complete conversion was reached. Sulfur profiles were measured using electron probe microanalysis and were found to agree quite closely with the grain model predictions in the low temperature range.

The grain model for nonlinear kinetics has been presented by Sohn and Szekely (1973b) for the case of a reaction following Langmuir-Hinshelwood rate law.

MODELING OF STRUCTURAL CHANGES DUE TO REACTION

A number of structural changes occur in the solid during the course of reaction and a realistic model for gas-solid reactions should account for these changes. The main reason to incorporate these into the model is that existing models cannot predict certain special behavior patterns which have been observed experimentally. Some of these are: (a) leveling-off of conversion-time data far below complete conversion; (b) existence of maxima in the rate-time data especially for gasification reactions; and (c) strong dependence of the reactivity of the solid on pore-size distribution.

The main structural changes are due to chemical reaction and sintering. This section analyzes the effect of changes due to reaction while effects of sintering will be presented in the next section. The changes due to reaction are mainly caused by the differences in the molal volume of the reactant and the product. This causes a change in the porosity of the solid and in the effective diffusivity. A number of attempts have been made to model these effects, and Table 3 presents a summary of most of these. A comparison of some of these models has been presented by Lindner and Simonsson (1981). A discussion of the main classes of models to account for structural changes due to reaction is presented below.

Modified Volume Reaction Models

In these models the porosity is assumed to change with local solid conversion according to some proposed empirical equation. A commonly used relation is a linear increase or decrease of porosity with conversion,

$$\epsilon = \epsilon_0 + \alpha_1(1 - B/B_o) \tag{21}$$

where ϵ_o is the initial porosity and α_1 is a constant. Corresponding to the porosity change the intraparticle diffusivity is assumed to change, and this again is represented by empirical or theoretical models. For example, if the random pore model of Wakao and Smith (1962) is used to describe the intraparticle diffusion, then the change in D_e can be represented as

$$\frac{D_e}{D_{eo}} = \left(\frac{\epsilon}{\epsilon_o}\right)^2 \tag{22}$$

where D_{eo} is the value of intraparticle diffusivity at time zero.

The model equations are then solved with varying diffusivity rather than with constant diffusivity. Other forms of equations of variation of D_e have been proposed by Wen (1968), Calvelo and Cunningham (1970), and Fan et al. (1977), and these are all empirical in nature. For instance, the relation used by Fan et al. (1977) is of the following form

$$D_e = D_{eo} \left\{ \frac{\alpha_2}{\exp\left[1 - \frac{1}{(B/B_o)^{\alpha_3}}\right] + \alpha_2^{-1}} \right] \tag{23}$$

where α_2 and α_3 are empirical constants. Computation using this form indicated a sigmoid conversion-time behaviour for certain ranges of parameters which is not generally predicted by a model with constant D_e. However it may be noted here that such an approach is purely empirical and does not lead to a detailed understanding of the effect of structural changes. Also the sigmoid behavior of conversion may be due to nucleation effects as discussed later.

Modified Particle-Pellet Models

In these models the radius of the grain r_G is assumed to change due to the differences in the molal volume of the products and reactants. A schematic representation of this model is shown in Figure 2. The change in radius of the particle can be easily related by the following equation:

$$r_G = [r_{Gt} + z_v (r_{Go}^3 - r_{Gt}^3)]^{1/3} \tag{24}$$

where r_G is the grain size at time t and r_{Go} is the initial grain size and z_v is the ratio of the molal volume of the product to the reactant defined as

$$z_v = \frac{\nu_G \, \rho_B \, M_G}{\nu_B \rho_G (1 - \epsilon_G) M_B} \tag{25}$$

The parameter z_v determines the changes in particle (grain) dimensions. If $z_v < 1$, the particles shrink during reaction; if $z_v > 1$, swelling occurs; for $z_v = 1$, there is no change in particle size as reaction progresses.

The porosity changes in the pellet can be related to changes in the particle size by the following equation:

$$\frac{1 - \epsilon}{1 - \epsilon_0} = \left(\frac{r_G}{r_{Go}}\right)^3 \tag{26}$$

The change in the diffusivity can be assumed to be proportional to ϵ^2 and this can be incorporated in the model equations. An illustrative result for an isothermal system is shown in Figure 3. The conversion levels off to an asymptotic value (which is less than 100%) for some cases when $z_v > 1$. Such incomplete conversions have been experimentally observed for reaction of SO_2 with limestone (Hartman and Coughlin, 1974, 1976) and in the hydrofluorination of UO_2 (Costa and Smith, 1971). The models which

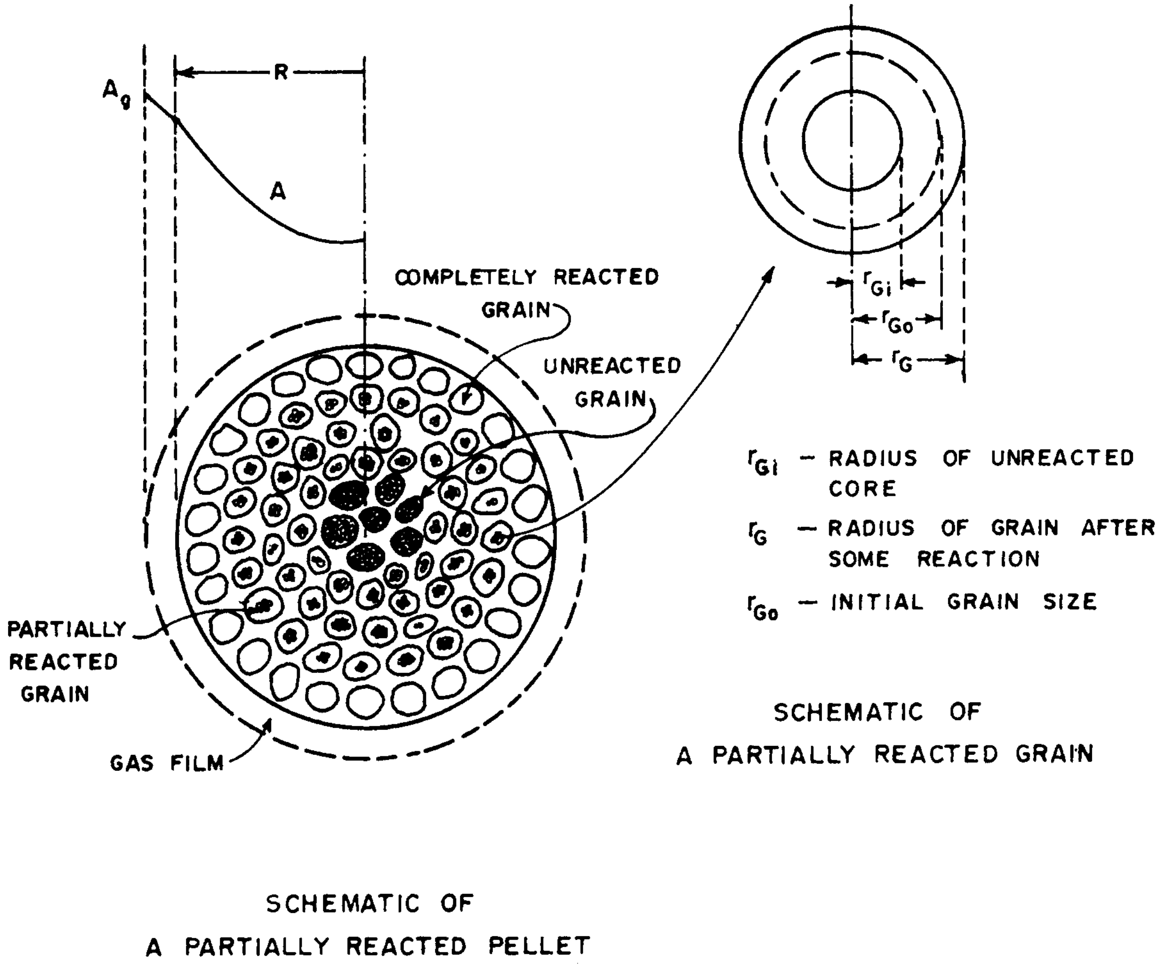

Figure 2. Schematic representation of the changing grain size model.

incorporate structural changes (particle size change in this case) are capable of predicting this phenomenon as can be seen from Figure 3. Incomplete conversion occurs when the porosity at the surface of the pellet becomes zero (pore closure phenomenon). An analytical equation can be derived from the dimensionless time required to reach pore closure (Georgakis et al., 1979):

$$\tau_{1,P} = \frac{1}{\mathrm{Bi}_p}\left[\frac{z_v}{z_v - 1} - \frac{1}{(1-\epsilon_o)^{2/3}}\left\{1 + \frac{z_v}{1 - z_v}\,\epsilon_0\right\}^{2/3} - \frac{1}{z_v - 1}\cdot\frac{1}{(1-\epsilon_o)^{2/3}}\right] + 1 - \frac{1}{(1-\epsilon_o)^{1/3}} \times \left[1 + \frac{z_v}{1 - z_v}\,\epsilon_0\right]^{1/3} \qquad (27)$$

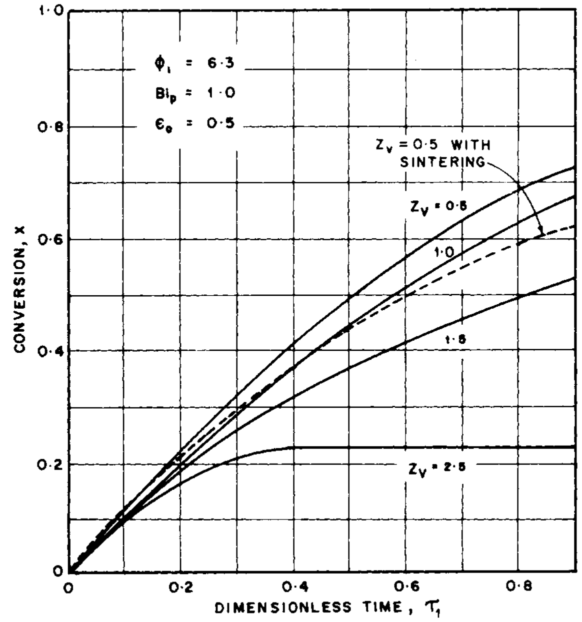

Figure 3. Effect of molal volume ratio parameter z_v on conversion based on changing grain-size model (Ramachandran and Smith, 1977b).

Also the maximum conversion of the solid is given by the following equation when $z_v > 1$ (Ramachandran and Smith, 1977a):

$$x_{\max} = \frac{\epsilon_o}{(z_v - 1)(1 - \epsilon_o)} \qquad (28)$$

From Eq. 28 it is also seen that if ϵ_o is greater than $(z_v - 1)/z_v$ then complete conversion of the solid is possible; otherwise the phenomenon of pore closure will be observed. The modified particle-pellet model has been used for the interpretation of experimental data on hydrofluorination of UO_2 (Ramachandran and Smith, 1977b) and sulfation of limestone (Georgakis et al., 1979). Both these systems have z_v values around three and hence exhibit the phenomenon of pore closure.

A variable property grain model has been proposed by Ranade and Harrison (1981) in a recent paper which is similar in concept to the model discussed above. In this model, the grain radius is assumed to vary under the combined influence of chemical reaction and sintering. Significant improvements in the match with the experimental data of the reaction of hydrogen sulfide with zinc oxide as compared to the constant property grain model have been achieved.

Single-Pore Models

The single pore models approach the problem in an entirely

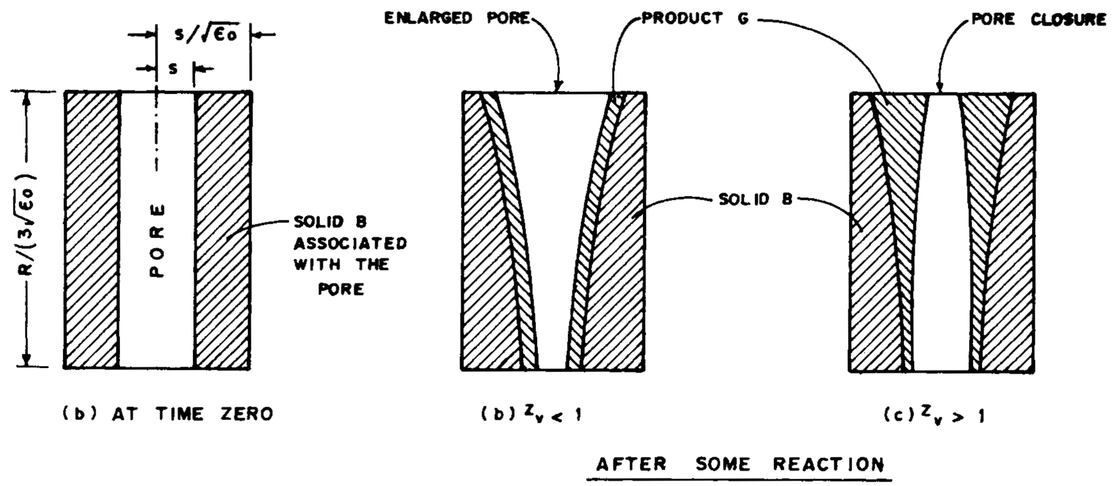

Figure 4. Schematic representation of the single-pore model.

different manner. In this case the model focusses attention on the changes taking place in a single pore which is supposed to be representative of the changes taking place in the pellet. The single pore can be assumed to be cylindrical with a concentric ring of solid B associated with it. A schematic representation of this is shown in Figure 4. The effect of structural changes would lead to an open pore structure as shown in Figure 4b for the case of $z_v < 1$. When $z_v = 1$ the pore geometry does not change with time. Finally for the case of $z_v > 1$, a decrease in pore size results as shown in Figure 4c and large values of z_v can lead to pore closure phenomenon. The model parameters are: (1) average pore radius; (2) radius of the associated solid; (3) effective pore length; (4) effective diffusivity through product layer; and (5) reaction rate constant. The first three parameters can be obtained independently by measuring the surface area and the pore volume of the initial pellet. Thus the main advantage of this model is the small number of independent model parameters. The model explains the results of sulfation of calcium oxide satisfactorily (Ramachandran and Smith, 1977a; Chrostowski and Georgakis, 1978). A disadvantage of the model is that it does not take into account the intersections of the reaction surfaces as the various pores present in the pellet react. This effect becomes important only after some appreciable conversion has occurred. Also the model does not take into account the pore size distribution which normally exists.

An extension of the single pore model to account for the effect of bulk flow and reversibility of the reaction has been proposed by Ulrichson and Mahoney (1980). Such a situation occurs for example in the chlorination of MgO and the model accounting for the above additional complexities fit the data more adequately.

Lee (1980) has analyzed a parallel pore model and obtained analytical solution for x-t behavior by an averaging technique. The model is similar in concept to the single pore model and the analytical relations developed by Lee are valid for low and intermediate values of Thiele modulus.

Distributed Pore Models

These models are similar in concept to the single-pore model but take into account the effect of pore-size distribution. Some of the recent approaches proposed in the literature are discussed below.

Christman and Edgar (1980) applied the single pore model locally at a point, r, in the pellet and for a pore of radius s_1. This pore is assumed to be covered with an inner concentric product layer of thickness $(s_2 - s_1)$. The reaction interface is thus a cylindrical surface at s_2. At time $t = 0$, $s_1 = s_{10}$ (the initial pore radius) and $s_2 = 0$. The values of s_1 and s_2 at any time are related by an equation which is the same as that for a single pore model.

$$s_1^2 = z_v s_{10}^2 + (1 - z_v) s_2^2 \tag{29}$$

The rate of reaction in kmol/s for this single pore is:

$$r_A^1(s_1, r, t) = \frac{2\pi(\Delta r/\tau_f)k_s s_2 A}{1 + \dfrac{k_s s_2}{D_{eG}} ln\left(\dfrac{s_2}{s_1}\right)} \tag{30}$$

where Δr is the length of a differential element in the pellet and the factor τ_f is introduced to account for the fact that not all pores are oriented in the radial direction. A value of $\tau_f = 3$ can be used for practical purposes as suggested by Johnson and Stewart (1965).

The average rate of reaction at position r is obtained by integrating Eq. 30 for the entire pore-size distribution. When this average value and an average value for effective diffusivity are incorporated into the mass balance we obtain

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\overline{D}_e\frac{dA}{dr}\right) = \bar{k}\,A \tag{31}$$

where $\overline{D}_e$ and $\bar{k}$ are the average values at position r defined as

$$\overline{D}_e = \frac{1}{\tau_f^2}\int_0^\infty \pi\, s_1^2\left[\frac{1}{D_M} + \frac{1}{D_k(s_1)}\right]^{-1} f(s_1)ds_1 \tag{32}$$

and

$$\bar{k} = 2k_s\int_0^\infty \frac{\pi s_2 f(s)_1)ds_1}{1 + \dfrac{s_2 k_s}{D_{eG}}\ln\left(\dfrac{s_2}{s_1}\right)} \tag{33}$$

Here the pore-size distribution is represented by the function $f(s_1)$ which is defined such that $f(s_1, r, t)ds_1$ represents the number of pores of sizes between s_1 and $s_1 + ds_1$ intersecting a unit surface at position r at time t. The pore size distribution itself changes with time and this was modeled in the work of Christman and Edgar (1980) by a population balance equation of the type

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial s_1}\left[f\frac{ds_1}{dt}\right] = 0 \tag{34}$$

Equation 34 is the standard population balance equation which assumes that there is no net fractional increase in the number of pores by "birth" or "death" mechanisms; that is, it assumes that the total number of pores are conserved. In reaction systems where a solid product is formed, there is no mechanism by which two pores may intersect to produce new pores. Hence the "birth" mechanism is absent. (This is unlike the case of gasification systems where the "birth" mechanism may also be present.) However pores can be lost by collisions; that is, if two pores are close enough for their outer radii of reaction to touch each other, part of the reaction surface is lost. Incorporation of this will generalize the model considerably but will require a complicated and exhaustive analysis of the problem which does not appear to have been made. A key feature of the approach of Christman and Edgar (1980) is that the evolution of the pore structure with time and position can be predicted. Thus we obtain additional information from the model such

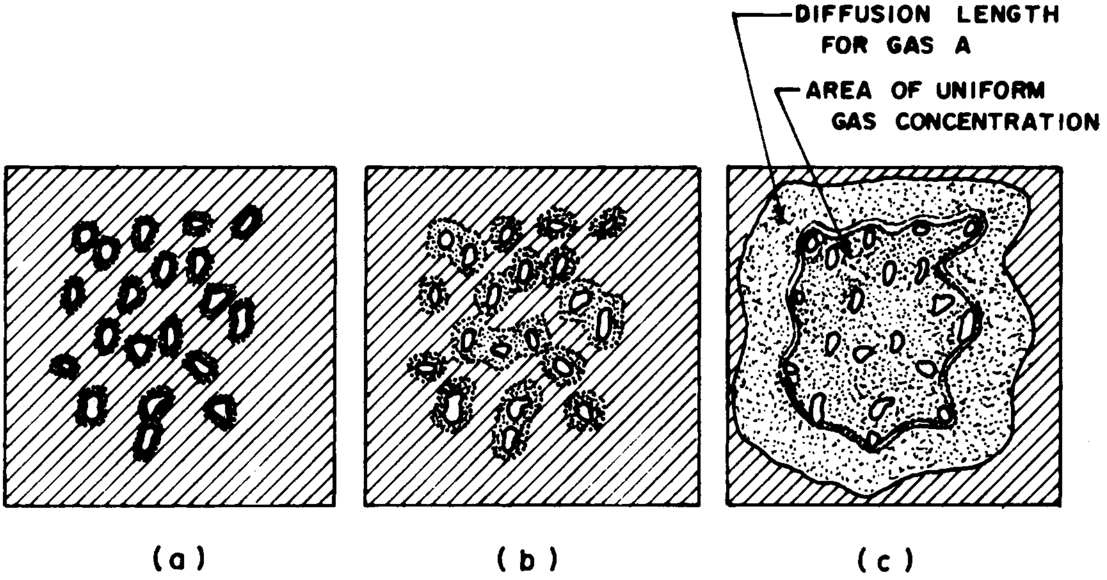

Figure 5. Development of reaction surface according to the random pore model. The shaded area represents unreacted solid B. The dotted area represents the product layer: (a) early stage showing product layer around each pore; (b) intermediate stage, showing some overlapping reaction surfaces; and (c) later stage, showing full development of product layer and reaction surface for the particular view chosen (Bhatia and Perlmutter, 1981a).

as pore-size distribution at various stages of reaction, and this can be matched with experiments for a rational verification of the model.

Simons and Rawlins (1980) followed a somewhat different approach to model the effect of pore-size distribution. They postulated that each pore in the pellet reaches the surface as a trunk of a tree. Thus the external surface of the pellet may be assumed to have a number of holes (or pores) with radii in the range of $s_{\min} < s < s_{\max}$. A number density function can be defined accordingly. Thus the number of pores opening at the surface whose radius is between s and s + ds is given by $4\pi R^2 f(s)ds$. The models can then be developed for each pore of radius s and then averaged over the surface pore size distribution to obtain the average flux of the gaseous reactant at the surface. This flux can in turn be related to the average conversion of solid B. For each pore of radius s, Simons and Finson (1979) ascribed an associated internal surface area defined by the equation

$$S_p = \frac{2\pi K_o s^3(1-\epsilon)}{\epsilon^{1/3}\, s_{\min}} \tag{35}$$

where K_o is a constant called as the pore aspect ratio which is assigned a value around five. The pore size distribution function $f(s)$ can be described by a suitable mathematical function to complete the definition of the problem. This will, of course, depend on the characteristics of the solid. Simons and Rawlins (1980) used the following type of relation:

$$f(s) = \frac{\epsilon}{2\, ln \left(\dfrac{s_{\max}}{s_{\min}}\right) \pi s^3} \tag{36}$$

The model is mathematically simple to use and has been used in the interpretation of the initial rate data for the reaction of SO_2 and H_2S with calcined limestone (Simons and Rawlins, 1980) and char gasification (Lewis and Simons, 1979).

Recently Bhatia and Perlmutter (1980, 1981a, 1981b) have proposed a model which takes into account the intersection of the pores as reaction proceeds. The model is called the random pore model and it assumes that the actual reaction surface of solid B to be formed by a randomly overlapping set of cylindrical surfaces of size distribution $g(s)$ where $g(s)$ ds is the total length of cylindrical surfaces (per unit volume of space) having radii between s and $s + ds$. A schematic diagram of the model is shown in Figure 5 which depicts the product layer surrounding the pores at different stages of the reaction. Bhatia and Perlmutter (1980) have derived equations for non-overlapped surface and volume of the reaction surface with conversion. The authors then related these to the actual (or overlapped) surface by an equation similar to that of Avrami (1940). Based on this model Bhatia and Perlmutter (1980) derived the following equation for the conversion-time behavior for the case of kinetic control:

$$\frac{dx}{d\tau_2} = (1-x)[1 - \Psi\, ln\, (1-x)]^{1/2} \tag{37}$$

where

τ_2 is a dimensionless time defined as $\dfrac{k_s A_g^m S_o t}{1-\epsilon_o}$

and Ψ is a structural parameter defined as

$$\Psi = 4\pi L_o(1-\epsilon_o)/S_o^2 \tag{38}$$

where S_o and L_o are the reaction surface and total length of the pore per unit pellet volume at time zero. Equation 37 is similar to other models; for example, if $\Psi = 0$ it reduces to the volume reaction model with $n = 1$. Similarly the grain model behavior can be closely approximated if $\Psi = 1$. This also leads to the conclusion that the concept of reaction order with respect to solid is closely related to the structure of the pores of the solid. A relation between the order of reaction n and the structural parameter Ψ has also been obtained and this is shown graphically in Figure 6. Thus the random pore model is able to offer a rational meaning to the reaction order with respect to the solid.

In subsequent papers Bhatia and Perlmutter (1981a, 1981b) extended this to consider the case of ash diffusion. The equation for conversion-time behavior at any point in the pellet was derived as

$$\frac{dx}{d\tau_2} = \frac{a\,(1-x)[1 - \Psi\, ln\, (1-x)]^{1/2}}{1 + \dfrac{2k_s\rho_B(1-\epsilon_o)}{\nu_B M_B D_{eG} S_o}\dfrac{z_v}{\Psi}\left[\sqrt{1 - \Psi\, ln\, (1-x)} - 1\right]} \tag{39}$$

This was incorporated into the diffusion equation for gas A in the pellet and the results were compared with the experimental data of Borgwardt (1970) on reaction of SO_2 with limestones. The model agreed with experimental data over a wide range of temperatures.

The model thus introduces one parameter Ψ to account for the pore-size distribution of the solid. Bhatia and Perlmutter (1981b) have derived equations for Ψ for various types of pore-size distribution such as bimodal, square, triangular, log-normal, normal, etc. For pores of uniform size the value of Ψ is shown to be

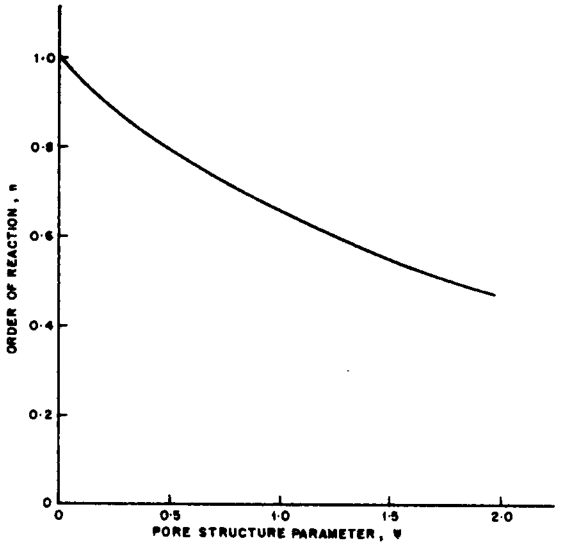

Figure 6. Relationship between the structural parameter of the random pore model and the order of reaction with respect to solid in the volume reaction model (Bhatia and Perlmutter, 1980).

$$\Psi = -\frac{1}{ln\,(1 - \epsilon_o)} \tag{40}$$

while for the general case

$$\Psi = \frac{4\pi \int_0^\infty g(s)\,ds}{\left[2\pi \int_0^\infty sg(s)ds\right]^2} \tag{41}$$

Further, an analysis of the various pore-size distributions indicates that a uniform pore size leads to the lowest reactivity. For a bimodal pore-size distribution an optimum structure exists for which reactivity is maximum. This may give useful guidelines in pellet preparation by compaction of microporous particles to yield a solid of maximum reactivity. Another interesting feature of this model is that for certain pore characteristics a rate maximum may be observed with increasing conversion. This maximum is ascribed to the growth of larger reaction surfaces from initially smaller pores. At later stages this is overshadowed by intersections of these growing surfaces. The model proposed by Bhatia and Perlmutter is sufficiently general and predicts much of the observed experimental behavior. It also tends to unify the various models such as volume reaction model and grain model in terms of basic structural parameters.

EFFECTS OF SINTERING

Many noncatalytic reactions are accompanied by large temperature rise in the pellet and this can cause sintering of the pellet. Sintering causes a decrease in the effective diffusivity of the pellet and this must be accounted for in the modeling of processes where sintering is likely to be important. Evans et al. (1973) accounted for this by assuming an exponential decay in the effective diffusivity with reaction time.

Ramachandran and Smith (1977b) have accounted for the effect of sintering on the rate of reaction based on the grain model. The basis for this modeling was an earlier study by Kim and Smith (1974) who measured the effective diffusivity in nickel oxide pellets during various stages of reduction. Both sintered and unsintered pellets were used in their study. These authors proposed a model for decrease in D_e due to sintering. According to this model, the primary influence of sintering is to decrease the pore interconnections. This causes a decrease in porosity of the pellet and a drastic increase in the tortuosity factor τ_f of the pellet. This increase in τ_f is not only due to the decrease in the porosity of the pellet but also due to removal of some pore interconnections. The fractional increase in tortuosity was correlated by Kim and Smith (1974) as a function of the fractions f_p of the pores removed:

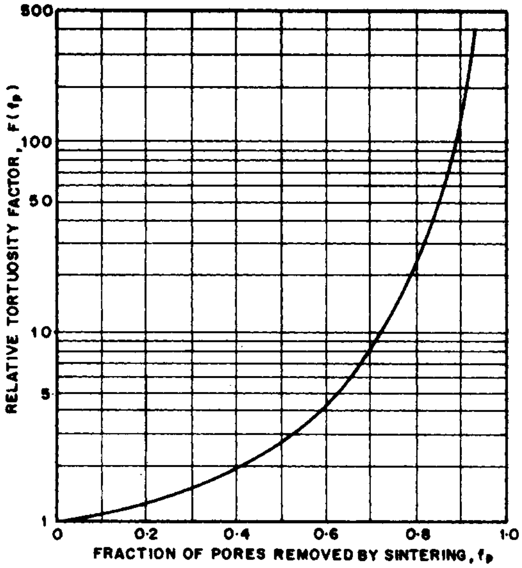

Figure 7. The effect of pore interconnections on the tortuosity factors (Kim and Smith, 1974).

$$F(f_p) = \frac{\tau_f(f_p)}{\tau_f(o)} \tag{42}$$

where $\tau_f(f_p)$ is the tortuosity factor when a fraction f_p of the pores are removed and $\tau_f(o)$ is the factor for $f_p = 0$. The correlation for $F(f_p)$ as a function of f_p developed on a theoretical basis by Kim and Smith is shown in Figure 7. A more complicated model for predicting the effect of sintering on the tortuosity factor has been developed by Chan and Smith (1976).

The change in effective diffusivity in the pellet due to the combined effect of chemical reaction and sintering was correlated by Ramachandran and Smith (1977b) by the following equation:

$$D_e = \left[\frac{1}{D_M} + \frac{1}{D_k}\right]^{-1} \frac{1}{F(f_p)} \left[1 - (1 - \epsilon_o)\left(\frac{r_{Gt}}{r_{Go}}\right)^3\right]^2 (1 - f_p) \tag{43}$$

The only additional information required for the modeling of the effect of sintering is the variation of f_p with time. Ramachandran and Smith (1977b) modeled this as a first order process thus:

$$\frac{df_p}{dt} = (1 - f_p)A_{f_p} \exp\left[\frac{-E_s}{R_g(T - T_m)}\right] \tag{44}$$

where E_s is the activation energy for sintering and T_M is a characteristic temperature corresponding to the onset of sintering. Generally T_M will correspond to the Tamman temperature which is approximately half the melting point of the solid. The model parameters introduced to account for the effect of sintering are A_{f_p}, E_s and T_M and these can probably be estimated by independent sintering measurements on the solid, i.e., by measuring the porosity and the effective diffusivity for various sintering times.

An illustrative result of the effect of sintering on the conversion-time behavior of an isothermal system is shown in Figure 3 for the case of $z_v = 0.5$ (as dotted line). In this case normally pore closure is not expected due to chemical reaction as the parameter z_v is less than unity. However the pore closure occurs due to the effect of sintering and results in incomplete conversion of the solid as shown in Figure 3.

Ranade and Harrison (1979, 1981) approached the problem of sintering effects in a different manner. In this model the sintering process is visualized to result in the combination of adjacent grains; the large number of small grains are assumed to be gradually replaced by fewer of large radius. The change in grain size is related to specific surface area of the grains which is described as a function of time by a rate law proposed by Nicholson (1965) (first-order decay in surface area). The model has been applied to the experimental results on the reaction of hydrogen sulfide with zinc oxide.

DECOMPOSITION REACTIONS

Decomposition reactions are of prime importance in many operations such as calcination, preparation of high surface area metal oxides, etc. These reactions may be represented as:

$$A_{(s)} \rightarrow G_{(s)} + P_{(g)} \tag{ii}$$

The decomposition reactions are modeled generally in terms of the sharp interface model and the rate of decomposition is assumed to be controlled by simultaneous transfer of mass away from and heat to the interface which separates the reactant and decomposed solid (Narsimhan, 1961; Hills, 1968; Campbell et al., 1970). At the decomposition interface, the concentration of the gaseous product P is assumed to be determined by the equilibrium of reaction (Eq. ii).

The model equations and results for conversion and temperature of the decomposing solid as a function of time have been well documented in the literature. In a recent paper Mu and Perlmutter (1980) modified these models to take into account the effect of changes in pellet size arising from possible density differences between reactant and product. Further in this work the effective diffusion coefficient of the product gas in the product layer (D_{eG}) was assumed to vary with the decomposition temperature T. The specific relationship of D_{eG} vs. T depends on the diffusion mechanism prevailing in the solid pores. If the diffusion mechanism is of the Knudsen type, D_{eG} is proportional to $T^{1/2}$, while for ordinary molecular diffusion the exponent of T is in the range of 1.5 to 2.0. The computational results of Mu and Perlmutter (1980) showed that the effects due to changes in particle dimensions were more significant than those due to the variation of D_{eG} with temperature. In another recent study, Prasannan et al. (1982) incorporated the effects of nonequimolal diffusion of the product gas on the rate of decomposition. The effects are not important if the diffusion is in the Knudsen regime, while if the process is controlled by bulk diffusion the analysis of the problem should include these effects.

Gokhale et al. (1975) reported some interesting observations on the disproportionation of potassium benzoate to terephthalate (used in the manufacture of polyester intermediates) and benzene.

$$2\ C_6H_5COOK \rightarrow C_6H_5(COOK)_2 + C_6H_6 \tag{iii}$$

The reaction with these pellets always started at the center and expanded radially outward. A delayed diffusion model has been proposed by Kulkarni and Doraiswamy (1980) to explain these unusual observations. In this model the reaction is assumed to take place in two steps with CO_2 being formed as an intermediate in the first step: The second step requires a critical partial pressure of CO_2 which is first reached at the point of symmetry in the pellet. This explains the initiation of the reaction (second step) at the center. An analytical solution for the rate of movement of the reaction interface radially outwards has been given by the same authors.

An industrially important class of decomposition reactions occurs in coal devolatilization or pyrolysis. These may be represented as

$$\text{Coal} \rightarrow \text{Residues} + \text{Volatiles} \tag{iv}$$

although the actual process is very complex involving the formation of several intermediates as pointed out in a review by Anthony and Howard (1976). The volatiles which are formed during heating of coal diffuses outward and as some of these are highly reactive free radicals they undergo secondary reactions in the pores of the solid. A model for intraparticle mass transfer effects in coal pyrolysis has been proposed by Gavalas and Wilks (1980). Although the detailed chemistry of the process is not well understood, the model proposed by these authors lumps the diffusing molecules into three species: tar, gases and inerts. The concentration profiles of these species are then evaluated by describing the process by ternary diffusion and viscous flow in conjunction with a simple pore model for coal. The model has been compared with some limited experimental data on subbituminous coal.

MISCELLANEOUS MODELS

Crackling Core Model

Park and Levenspiel (1975) proposed the so-called crackling core model to account for the sigmoidal behavior of x vs. t plots in some observed systems. In this model the reaction is assumed to occur in two steps:

$$(1)\ A\ (\text{nonporous}) \xrightarrow{\text{Physical change}} A\ (\text{porous}) \tag{v}$$

$$(2)\ A\ (\text{porous}) \rightarrow \text{product} \tag{vi}$$

The first stage is a physical transformation of A from a nonporous structure to a more reactive porous structure which then undergoes reaction according to the second step. The model can also be used to represent a situation where the reaction of solid occurs in two consecutive steps. For example, in the reduction of hematite the steps are

$$Fe_3O_4 \xrightarrow{+H_2} Fe_2O_3 \xrightarrow{+H_2} FeO \xrightarrow{+H_2} Fe \tag{vii}$$

The first step results in the formation of a porous structure which undergoes further reaction. Similar sequence occurs in the reduction by hydrogen of manganese oxide (De Bruijn et al., 1980).

$$MnO_2 \xrightarrow{H_2} Mn_2O_3 \xrightarrow{H_2} Mn_3O_4 \xrightarrow{H_2} MnO \tag{viii}$$

The crackling core model has been successfully used in the interpretation of experimental data in such systems. Although the model can predict the qualitative features of these systems reasonably well, it is only an approximation and does not consider the basic mechanisms responsible for the sigmoidal behavior: One such effect could be the nucleation effect which is discussed below.

Nucleation Models

Nucleation effects are often significant in some gas-solid reactions such as reduction of metallic oxides. Typical x-t behavior at low temperatures for these systems shows three periods: (a) induction period; (b) acceleratory period; and (c) decaying period. These three stages arise from the following succession of events: (1) formation of nuclei of the metallic phase at localized sites on the oxide surface; (2) growth of these nuclei; and (3) overlap of the growing nuclei and a decrease in the metal/oxide interface. The length of the induction period is most intimately connected with the rate of formation of nuclei. If the nuclei are formed fast (as is the case at high reaction temperature or when the surface-to-volume ratio is small) the entire surface gets covered rapidly with the metallic phase and a metal/oxide interface develops. The reaction then proceeds in a topochemical manner. On the other hand, if the rate of nucleation is not very large, the metal/oxide interface will be irregular. The mathematical modeling of product layer diffusion and chemical reaction for these two distinct situations is, of course, quite different. Some aspects of these have been discussed by Sohn (1978) and Rao (1979). Formation and growth of nuclei in the H_2 reduction of wüstite has been observed by El-Rahaiby and Rao (1979).

A rate equation has been developed by Avrami (1939, 1940, 1941) for the x-t relationship in the absence of pore diffusion:

$$ln \left(\frac{1}{1-x}\right) = C' t^N \tag{45}$$

where C' and N are constants and N depends on the rate of formation of nuclei. A more general numerical solution of the problem has been presented by Ruckenstein and Vavanellos (1975) which includes both isothermal as well as nonisothermal systems. The classical Avrami Model has been modified by Bhatia and Perlmutter (1979) to include the initial volume of the nucleus and a population balance approach is used to model the solid-phase reactions in terms of nuclei of the product phase dispersed in the reactant matrix. A conversion-time relationship is obtained by the solution of a set of moment equations derived from the population balance. A model of nucleus impingement at low conversions is formulated and applied to published data on the oxidation of cuprous iodide.

The effect of pore diffusion on systems following nucleation kinetics of the type given by Eq. 45 has been analyzed by Sohn (1978). Approximate analytical solutions have also been presented assuming the law of addition of diffusion and reaction times.

Solid Catalyzed Gas-Solid Reactions

A number of gas-solid reactions are catalyzed by solids. Some industrially important examples are: (1) hydrogasification of coal and coal char catalyzed by alkali-metal or calcium compounds; and (2) formation of chlorosilanes (used in the manufacture of silicones) by reaction of methyl chloride and silicon catalyzed by metallic copper.

Detailed mathematical analysis is not available for these systems. Lee (1979) proposed a simple model for catalyzed gas-solid reactions on the assumption that the catalyst is present as an external layer surrounding the solid reactant. In this model the reactant gas is assumed to diffuse through this catalyst layer and the gasification of the solid reactant takes place at the catalyst/solid reactant interface. As conversion proceeds, the thickness of the catalyst layer increases causing the effectiveness factor to decrease. This model is a simplified picture and more complete modeling along with systematic experiments is necessary.

Guzman and Wolf (1979) also analyzed this problem assuming a nonuniform distribution of catalyst within the pellet. The theoretical analysis included two models of the pore structure and uniform, linear and parabolic activity profiles for the distribution of the catalyst. The results of the analysis revealed that in gas-solid reactions catalyzed by solids, nonuniform catalyst distribution is detrimental to solid conversion and efforts should be made to attain a uniform catalyst distribution.

Chloromethylation of silicon (or ferrosilicon) to form methyl chlorosilanes by copper catalyst is an industrially important system. A fluidized bed technology developed by the National Chemical Laboratory is in operation (Doraiswamy et al., 1980). Even though systematic modeling of this complex solid catalyzed gas-solid reaction has not so far been attempted, Voorhoeve (1967) has suggested a physical picture of the reaction mechanism which is given in Figure 8. The reaction is catalyzed by η-Cu_3Si, which is formed during the initial stages of the reaction.

This initial solid-solid reaction was found to be autocatalytic by Tamhankar et al. (1981a). Silicon from the η-phase then reacts with methylchloride and leaves the lattice as gaseous product. The vacant lattice site is occupied by silicon diffusing from the silicon phase to the η-phase. The silicon conversion is limited by the blocking of the silicon surface by the η-phase, whereby the rate of solid state diffusion of silicon to the copper-rich surface becomes the rate limiting step. The above physical model can form the starting point for a detailed mathematical modeling of the process.

GASIFICATION REACTIONS

In gasification type of reactions only gaseous products are formed. Examples of such reactions are found in the combustion of carbon, formation of metal carbonyls, etc. The analysis of such reactions for nonporous particles can be approached using the

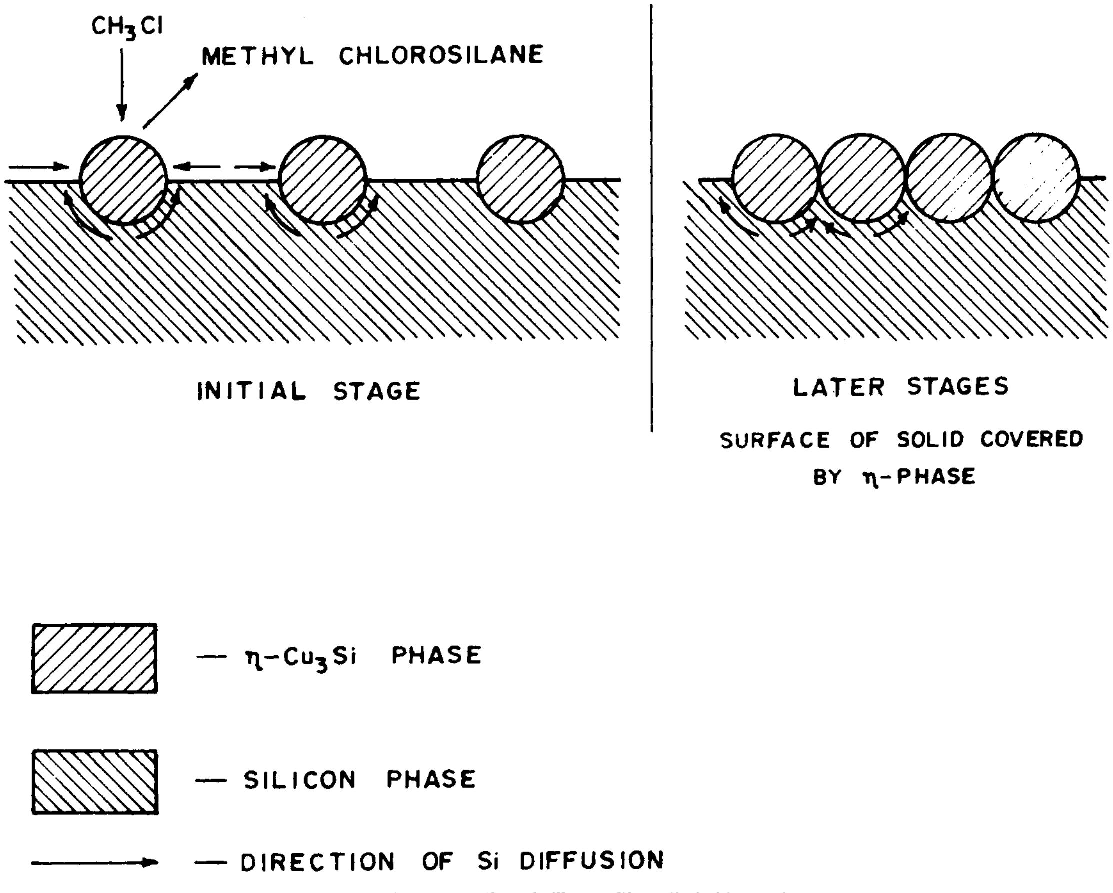

Figure 8. A physical model for reaction of silicon with methyl chloride (Voorhoeve, 1967).

shrinking core model. This has been attempted by Szekely et al. (1976) and Levenspiel (1973). The main feature of the analysis of gasification reactions on the basis of the sharp interface model is that no product layer exists, and hence diffusion through the ash layer which exists in the general type of reactions (Eq. i) is not present.

For porous particles the change in surface area with reaction must be considered. The gasification reactions provide a case of severe structural changes as no solid product is formed during the reaction. In some cases gasification may only be partial (chars to activated carbon) but even here the structural changes are very significant.

One of the first models to explain this problem was proposed by Petersen (1957) who assumed a random distribution of uniform-sized pores. A method was presented for the analysis of this type of reaction where the kinetic expression is linear in concentration of the reacting gas and where appreciable concentration gradients are established in the pore system as a result of intraparticle diffusion.

The model of Petersen leads to the following equation for the gasification reaction of a porous pellet in the absence of intraparticle gradients. (Szekely et al., 1976)

$$x = \frac{\epsilon_0}{1-\epsilon_0}\left[\left(1+\frac{k_s A_g^m t}{s_{po}}\right)^2 \frac{\left(G'-1-\frac{k_s A_g^m t}{s_{po}}\right)}{G'-1} - 1\right] \tag{46}$$

where G' is the solution of the cubic equation

$$\frac{4}{27}\epsilon_0 G'^3 - G' + 1 = 0 \tag{47}$$

and s_{po} and ϵ_o is the initial pore radius and porosity respectively.

Hashimoto and Silveston (1973a, b) modeled the gasification reaction on a microscopic scale by allowing for pore growth, initiation of new pores and coalescence of adjoining pores. Each of these leads to change in number of pores of a particular size and of the pore size density distribution function. These changes were modeled on the basis of a population balance equation of the following form:

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial s}\left(f\frac{ds}{dt}\right) - B' + D' = 0 \tag{48}$$

where B' is the rate of introduction of new pores of size s and D' is the rate of removal of such pores by coalescence. Equation 48 was converted into a set of differential equations by the method of moments (i.e., multiplying by s^n and integrating from 0 to s). The equation was then coupled with a rate model of the form

$$\frac{ds}{dt} = \frac{k_1 M_B A}{\rho_B} \tag{49}$$

This coupled with suitable equations for the rate of formation of new pores and rate of pore coalescence provides the complete formulation of the problem.

The effect of intraparticle diffusion was also considered in a subsequent paper. This could be characterized by a Thiele modulus $R_o[k_1\rho_B S_o\epsilon_o/\nu_B D_{eo}]^{1/2}$. If the modulus is greater than 10 the shrinking core model can be used, while if it is less than 0.1 diffusional gradients may be ignored in the model formulation. The model predicts a maximum in the relative surface area vs solid conversion behavior. The model needs large numbers of parameters to characterize the system and many of these can be obtained only by matching experimental data with theory.

Simons and Finson (1979) and Simons (1979) have also proposed a similar model. This model deals with various important quantities such as density of pore intersections, length of pore segments. In this model the gasification rate is calculated by integrating the rate of gasification per pore "tree" over the postulated pore-size distribution. (See the section on "Single-Pore Models.")

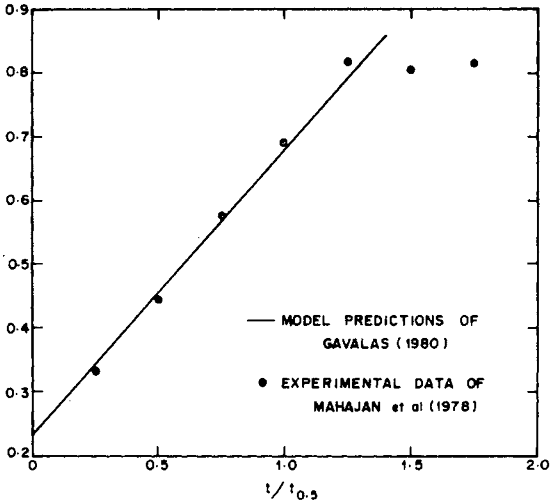

Figure 9. A comparison of the predictions of random capillary model with data on gasification of char.

In a recent study Gavalas (1980) has proposed a random capillary model for describing the porous medium. In this model the porous solid is described by a single probability density function $p(s)$ which is related but not identical to the customary pore size distribution. For low porosity this function is defined as follows:

$$p(s) = \frac{f(s)}{2\pi s^2} \tag{50}$$

Based on the probability distribution two structural parameters are defined

$$N_o = \int_{s_{\min}}^{s_{\max}} p(s_o)ds_o \tag{51}$$

$$N_1 = \int_{s_{\min}}^{s_{\max}} sp(s_o)ds_o \tag{52}$$

where $p(s_o)$ is the density distribution based on the initial pore-size distribution.

The model of Gavalas (1980) predicts the conversion-time pattern in terms of the above two structural parameters:

$$x(t) = 1 - \exp\left[-2\pi(N_o v^2 t^2 + 2N_1 vt)\right] \tag{53}$$

where v is the reaction velocity defined as the rate of change of pore radius with time.

A rearranged form of Eq. 53 indicates that a plot of $1/t\ ln\ 1/1 - x$ vs. t is a straight line with a slope equal to $2\pi N_o v^2$ and an intercept equal to $4\pi N_1 v$. Similarly by differentiating Eq. 53 and eliminating t the following linear equation is obtained:

$$\left[\frac{1}{4\pi(1-x)}\frac{dx}{dt}\right]^2 = \frac{N_o v^2}{2\pi} ln\left(\frac{1}{1-x}\right) + (N_1 v)^2 \tag{54}$$

These forms of linear equations are very convenient in correlating $x - t$ or (dx/dt) vs. x data and have been used by Gavalas (1980) to correlate the data of Mahajan et al. (1978) and Dutta and Wen (1977) on gasification of char by oxygen. The model comparison is shown in Figure 9. In the absence of a detailed characterization of the porous structure of char the parameters N_o and N_1 may be viewed as empirical correlating constants. Equation 53 also predicts a maximum in the reaction rate when the following value of conversion is reached.

$$x_{\max\ \mathrm{rate}} = 1 - \exp\left[-\left(\frac{1}{2} - 2\pi\frac{N_1^2}{N_o}\right)\right] \tag{55}$$

Such a maximum in the rate curve has been observed, for instance, by Dutta and Wen (1977) and the model of Gavalas correctly indicates this behavior.

The random pore model of Bhatia and Perlmutter (1980) can also be used to model gasification processes. (For such a system the molal volume parameter z_v approaches zero.) The model predicts a semilog relationship between the groups $[S/1-x]^2$ and $(1-x)$ and this is in conformity with the data of Hashimoto et al. (1979) on steam activation of char.

The kinetics of reaction of coal char with CO_2 was found to follow a nonlinear Langmuir-Hinshelwood relation by Dutta et al. (1977). Inclusion of this behaviour is necessary for a correct modeling of the process, especially when significant intraparticle gradients exist in the pellet.

A model for intraparticle diffusion effects in char combustion has been proposed by Srinivas and Amundson (1980a) incorporating the effects of three independent reactions

$$C+\frac{1}{2}O_2 \rightarrow CO \tag{ix}$$

$$CO+\frac{1}{2}O_2 \rightarrow CO_2 \tag{x}$$

$$CO_2 + C \rightarrow 2CO \tag{xi}$$

Based on the published literature kinetics, reactions ix and xi were found to be predominant. The model predicts the existence of three steady states under certain conditions. It does not however include the effects of structural changes. In a related study the process of char gasification was analyzed by Srinivas and Amundson (1980b). The process was assumed to consist of four independent reactions, namely, steam gasification, carbon dioxide gasification, hydrogasification and water gas shift reaction. A parametric study of the various factors affecting the gasification process has been presented by these authors.

COMPLEX GAS-SOLID REACTION SYSTEMS

The analysis in the earlier sections was mainly confined to the case where a simple single step reaction takes place. Many of the industrially important systems follow complex reaction schemes and modeling of these becomes correspondingly difficult. No generalized approach has been reported at this stage, and in this section we shall summarize the approaches followed for specific systems. In some cases the postulated physical models are presented, as these often provide the basis for further mathematical analysis of these problems.

Representative types of complex gas-solid systems with some important examples are presented in Table 4. A number of schemes have been analyzed on the basis of the sharp interface model by Wen and Wei (1971) for isothermal systems and Rehmat and Saxena (1977) for nonisothermal systems. The application of the zone model for complex reactions has been reported in a recent paper by Tone and Wen (1981).

Consecutive Reactions

These are encountered in the reduction of haematite by H_2 or CO. The reaction proceeds through the sequence indicated in Eq. vii. Hence complex models are necessary to represent this problem. Such models have been presented, for instance, by Spitzer et al. (1968) and Tsay et al. (1976), which account for the presence of three interfaces (Haematite/magnetite, magnetite/wüstite, wüstite/iron) in the pellet (Figure 10). Each step of the reaction is assumed to take place at the sharp interface separating the respective product and reactant. The application of other types of models and inclusion of structural changes appear to be an interesting possible future development in this area.

Reaction of Two Gases

Reaction of two gases with the same solid is encountered in a number of situations. Reduction of iron ores with a mixture of reducing gases such as CO and H_2 appears to be the most important problem belonging to this class. Here the existence of four gaseous components (CO, H_2, CO_2 and H_2O) necessitates the use of generalized Stafan-Maxwell equations to characterize the diffusion of the gases in the product layer. Such an approach has been followed by Tsay et al. (1976). The sharp interface model was again

TABLE 4. SOME EXAMPLES OF COMPLEX GAS-SOLID REACTIONS

Type	Scheme	Examples	Investigation
1	2	3	4
1. Consecutive Reactions of the Solid	$B \xrightarrow{+A} G_1 \xrightarrow{+A} G_2$	1. Reduction of Haematite	Spitzer et al. (1966)
		2. Reduction of Manganese Oxide	De Bruijin et al. (1980)
2. Consecutive Reactions of the Gas	$A_1 \xrightarrow{+B} P \xrightarrow{+B} G_2$	1. Reaction of Iron Sulfide with Oxygen	Tseng et al. (1981)
3. Reaction of Two Gases with the Same Solid	$A_1 + B \rightarrow$ Products $A_2 + B \rightarrow$ Products	1. Reduction of Iron Ore with a Mixture of CO and H_2	Tsay et al. (1976)
		2. Reaction of UO_2F_2 with a mixture of F_2 and BrF_5	Anastasia et al. (1971)
4. Reaction of Two Solids with the Same Gas	$A + B_1 \rightarrow$ Products	1. Chlorination of Ilmenite	Doraiswamy et al. (1959)
	$A + B_2 \rightarrow$ Products	2. Regeneration of Coked Catalyst	Ramachandran et al. (1975)
		3. Sulfation of Dolomite	Hartman and Coughlin (1976)
		4. Reduction of a Mixture of Nickel Oxide and Iron Oxide	Szekely and Hastaoglu (1976)
5. Gaseous product of first reaction reacting with a second solid	$A_1 + B_1 \rightarrow G + P$ $P = \nu_{A1}A_1 + B_2 \rightarrow$ Products	1. Reduction of cobalt sulfide in presence of CaO	Fahim and Ford (1978)
		2. Oxidation of metal sulfide in presence of CaO	Bartlett and Huang (1973)
6. Solid product of first reaction reacting with a second gas	$A_1 + B \rightarrow G + P$ $G + A_2 + \nu_{A1}A_1 \rightarrow$ Products	1. Simultaneous oxidation and sulfation of cuprous oxide	Bourgeois, Jr. et al (1974)
		2. Direct removal of $H_2S(A_2)$ from hot synthesis gas ($A1 = CO$; $A2 = H_2S$, $B = Fe_2O_3$; $G = Fe$)	Hasatani and Wen (1977) Tamhankar et al (1981b)
7. Homogeneous heterogeneous reactions	$A_g + B_s \rightarrow G + P$ $B(s) \rightarrow B(g)$ $A_g + B_g \rightarrow G + P$	1. Reduction of metal chlorides with hydrogen	Rao (1981)

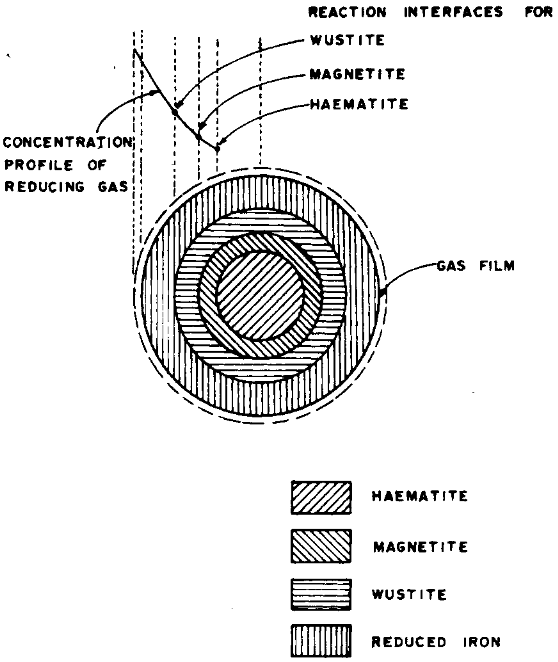

Figure 10. Three interface model for reduction of haematite (Tsay et al., 1976).

used as the basis for this development; the two gases diffuse to this sharp interface and react with the solid at this point. A key feature of this work is that multicomponent diffusional models have been used to describe the diffusion of the reacting and product gases in the ash layer. Croft (1979) has indicated that the possibility of water gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$) occurring in the product layer is likely and hence the effect of this reaction on the conversion-time behavior of the solid needs to be analyzed in detail. This may be of some importance as the product layer which is composed of reduced iron is an excellent catalyst for this reaction.

Sohn and Braun (1980) have developed a general model for reaction of two gases with the same solid.

Reaction of Two Components in the Solid

Reaction of two components present in the solid with the same gas occurs in a number of situations, for example, (a) chlorination of ilmenite, (b) sulfation of dolomite etc. In these cases generally one of the solids reacts more rapidly with the gas while the second component of the solid may not react or may undergo a slow reaction. These systems are again characterized by significant structural changes and future models should include these effects. An interesting example of reaction of two components of the solid is encountered in the burning of coke from catalyst particles. Here coke oxidation is considered to be composed of two steps: oxidation of hydrogen which occurs relatively rapidly in the initial time leaving behind a solid consisting of hydrogen depleted coke which gets oxidized subsequently. A model has been proposed for this process by Ramachandran et al. (1975). A schematic representation of this model is shown in Figure 11. The model predicts the experimentally observed rapid initial temperature rise in the pellet fairly well.

A more complex version of reaction of two solid components of the pellet occurs in the oxidation roasting of sulfide minerals in the presence of lime (a process of likely importance in view of the emphasis on pollution abatement). Here the gaseous product of the first reaction reacts with the second solid component. The systems may be schematically represented as

$$\frac{3}{2} O_2 + Me_x\,S \rightarrow SO_2 + Me_x\,O \qquad \text{(xii)}$$

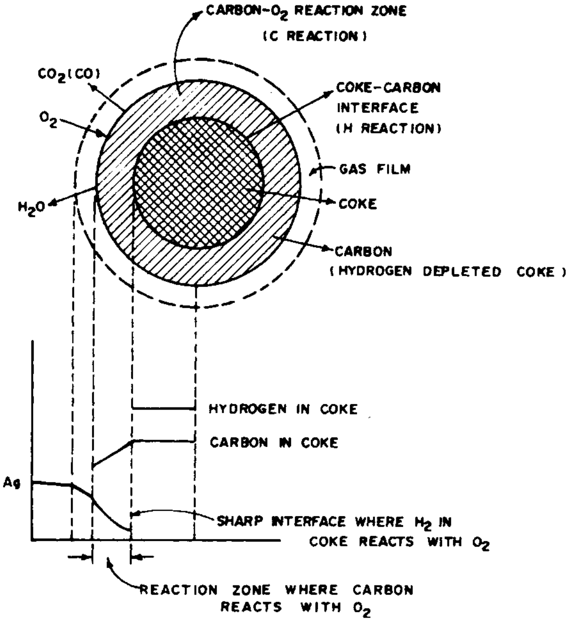

Figure 11. Model for simultaneous carbon and hydrogen reaction for coke oxidation (Ramachandran et al., 1975).

$$SO_2 + \frac{1}{2} O_2 + CaO \rightarrow CaSO_4 \qquad \text{(xiii)}$$

where *Me* represents a metallic element. A similar reaction sequence occurs in the reduction of metal sulfides in the presence of CaO

$$Me_x\,S + H_2 \rightarrow H_2S + x\,Me \qquad \text{(xiv)}$$

$$H_2S + CaO \rightarrow CaS + H_2O \qquad \text{(xv)}$$

Sohn and Rajamani (1977) have proposed a model for successive gas-solid reaction of these types. The model can be used to determine the optimum structure of the pellet and to provide useful guidelines for the design of experimental investigations of these reactions.

Fahim et al. (1978) proposed a model for metal sulfide reduction in the presence of CaO. In this model the pellet was assumed to consist of CaO and Me_x S grains. The latter were assumed to be nonporous while the CaO grains were assumed to be porous. Further each grain of CaO was assumed to consist of spherical non-porous sub-grains. The model equations were solved numerically and compared with experimental results in a subsequent paper (Fahim and Ford, 1978). In these types of reactions the kinetics of both reactions should be studied independently and these data should be used in modeling the overall process.

Solid-Solid Reactions with Gaseous Intermediates

An important class of complex reactions falls in the category of solid-solid reactions proceeding through gaseous intermediates. Reduction of metal oxides with carbon is a major example and the overall reaction may be represented as

$$Me0 + \frac{1+\nu}{2} C \rightleftharpoons Me + \nu CO + \frac{1-\nu}{2} CO_2 \qquad \text{(xvi)}$$

Although the above representation indicates that this is a solid-solid reaction, the actual mechanism is through a gaseous intermediate CO_2 and can be represented as

$$Me0 + CO \rightarrow Me + CO_2 \qquad \text{(xvii)}$$

$$CO_2 + C \rightleftharpoons 2CO \qquad \text{(xviii)}$$

A detailed description of modeling of such reactions has been described in the book by Szekely et al. (1976). A number of systems

TABLE 5. EXAMPLES OF SOLID-SOLID REACTIONS PROCEEDING THROUGH GASEOUS INTERMEDIATES

Reducing Solid	Metal Oxide	Reference
Graphite	Ferric Oxide	Otsuka and Kunii (1969)
Graphite	Ilmenite	El-Guindy and Davenport (1970)
Graphite	Silica	Klinger et al. (1966)
Carbon	Hematite	Rao (1971, 1974); Sohn and Szekely (1973a)
Carbon	Magnesium Oxide	Fruehan and Martonite (1976)
Carbon	Iron Oxide	Fruehan (1977)
Carbon	Manganese Oxide	Kor (1978)
Carbon	Stannic Oxide	Padilla and Sohn (1979)
Carbon	Ilmenite	Wouterlood (1979)
Carbon	Chromium (III) Oxide	Vodop'yanov et al. (1979)
Carbon	Zinc Oxide	Jalan and Rao (1977)
Carbon	Titanium Oxide	Barin and Schuler (1980)
Carbon	Zirconium Oxide	Biceroglu and Gauvin (1980)

of importance falling in this class have been investigated in recent years and most of these have been summarized in Table 5. The rate controlling step is often found to be reaction of carbon with CO_2 (for example, Kor, 1978). Two complexities arise in the modeling of these systems which could form interesting problems for future research: (1) The reaction of carbon with CO_2 follows nonlinear kinetics. For example, Turkdogan et al. (1970) observed the following type of rate law for oxidation of carbon

$$r_c = \frac{kp_{CO_2}}{1 + Kp_{CO}} \tag{56}$$

where k is the rate constant and K is the equilibrium constant for chemisorption of CO on the carbon surface. (2) The metal formed during reduction appears to have a catalytic effect on the reaction of carbon (for example, Padilla and Sohn, 1979). The incorporation of these effects on modeling of these systems may be useful.

A related problem occurs in the chlorination of oxides in the presence of carbon. This is of great importance in Zr and Ti metallurgy and the reaction may be represented as

$$MeO_2 + 2Cl_2 + 2C \rightarrow Me\,Cl_4 + 2CO \tag{xix}$$

where Me represents metals such as Zr, Ti, Al, etc.

The reaction thus involves reaction of two solid components and a gas. The products are generally gaseous under the reaction conditions and therefore it can be easily noted that severe structural changes occur during the reaction. The mechanism of the reaction is not very clear and there is considerable disagreement among various workers on this aspect. As a consequence detailed modeling of these types of reactions has not been attempted in the literature. Biceroglu and Gauvin (1980) have proposed a simplified model where the rate of reaction was assumed to be proportional to the initial carbon concentration, to the amount of unreacted zirconium dioxide left in the pellet and the chlorine partial pressure with an exponent of 0.7 to 0.8. Further, the degree of contact between the two solid constituents (MeO_2 and carbon) may influence the progress of reaction. Formation of activated atomic chlorine species on the carbon surface and subsequent diffusion and reaction of these on metal oxide surface has also been postulated as a possible reaction mechanism (Barin and Schuler, 1980). A detailed experimental investigation with a view to identifying the major rate controlling steps may be a prerequisite to a rational model development of these systems.

STABILITY OF GAS-SOLID REACTIONS

Understanding the region of stability of gas-solid noncatalytic reactions is important in interpretation of laboratory data, model verification and reactor design. Although considerable work has been done in analyzing the stability of gas-solid catalytic reactions the work in the area of noncatalytic reactions has been relatively sparse. One of the reasons is the mathematical difficulties arising out of the transient nature of the problem in contrast to the gas-solid catalytic system which attains a true steady state. In the following section a brief summary of the work done in this area is presented.

The instability occurring in gas-solid noncatalytic reactions may be classified into four major categories.

1. Geometric instability
2. Thermal instability
3. Transition in rate-controlling steps
4. Oscillatory instability

Geometric Instability

Geometric instability arises due to certain irregularities (such as thermocouples, void portions, etc.) in the pellet. When the rate of reaction decreases as the surface area reduces, the system is stable. In this case the effect of any surface irregularity is not felt and the reaction interface maintains the same initial shape (spherical in case of spherical pellet). If the reverse is true (rate increases with decreasing area) then the unevenness in the surface propagates and results in geometric instability. This was first pointed out by Cannon and Denbigh (1957). For isothermal first order systems the analysis of Nelson (1969) and Evans (1974) indicates that for minor surface irregularity the interface is stable and geometric instability exists only for large deformations (such as a cavity inside the pellet, etc.)

Thermal Instabilities

Thermal instabilities occur due to the linear nature of the rate of heat removal and the sigmoidal nature of the heat generation curves. The point of intersection of these curves represents the steady state (pseudosteady state for the case of reacting solids). Thus under certain conditions the pellet can operate in the region of multiple steady states. Criteria have been proposed in the literature for delineating this region by Shen and Smith (1963) and Aris (1967) for sharp interface models and by Calvelo and Smith (1970) for the particle-pellet model. In all these models a pseudo-steady state for heat transfer was assumed. Thus the effect of the heat capacity of the pellet was ignored, thereby rendering the results less useful practically. A general transient analysis of the problem may be necessary and some aspects have been investigated by Wen and Wang (1970).

The sudden transition in the controlling regime is a consequence of thermal instability. This means that the reaction rate accelerates suddenly at some point in time. This has important consequences in reactor operation as runaway conditions may occur. Also, a sudden decrease in the rate could be observed in some cases. Illustrations of this in systems of practical importance do not appear to have been published.

Oscillatory Behavior

Oscillatory instability has been observed in some systems due to some complex reaction mechanisms occurring in the solid. This is typically characterized by oscillations in the weight loss vs. time data. This has been observed in the reaction of ZnO with H_2S at high temperatures (Gibson and Harrison, 1980) and has been explained as being due to decomposition of ZnO at high temperatures. The Zn vapor produced in this decomposition diffuses outward and blocks the pore of the catalyst. Another example of this has been observed by Lynch and Elliott (1980) in the oxidation of CaS and has been explained as being due to the formation of $CaSO_4$ in the pores and its subsequent decomposition.

COMMENTS ON MODEL EVALUATION

From the discussions of the previous sections it is seen that a number of models have been proposed to predict the behavior of gas-solid noncatalytic reactions. However in order to evaluate the models critically and to apply them to systems of interest, a complete set of experimental data is necessary and this is often lacking in the literature. In this section we examine the type of data required and procedures for model evaluation.

An important conclusion that emerges from the previous sections is that the structure of the solid plays a key role in characterizing the rate of reaction. Hence a complete characterization of the solid must be undertaken in addition to obtaining the usual conversion-time data. This has not been the practice in some of the earlier studies and hence a critical comparison of various models using such data is rather difficult. The porosity and the pore size distribution of the solid turn out to be important parameters in many of the models and hence such measurements are of great importance. In addition, the characterization of the solid at various stages of reaction and that of the final product is often important. Such data are very valuable in fitting the models which predict the evolution of pore structure with time.

A second important quantity that can be determined from independent experiments is the effective intraparticle diffusivity. These can be measured under nonreacting conditions by a number of techniques. Such measurements should again be done for various extents of reaction in order to note any changes in the effective diffusivity as a function of the conversion of the solid.

In some systems sintering of the solid reactant or product occurs to a considerable extent. In these cases the effective diffusivities are significantly altered by the process of sintering; tortuosity factors of more than 100 have been experimentally reported for highly sintered pellets (Kim and Smith, 1977). For such systems diffusivity measurements for partly and fully sintered pellets are necessary. Also the rate of sintering must be determined by measuring some property such as surface area or porosity or pore size distribution as a function of time at various temperatures. Such data are needed to predict the effect of sintering on the conversion-time behaviour.

Determination of the order of reaction with respect to the gas is necessary for a complete model fitting. Such data can easily be obtained by varying the partial pressure of the gas phase species (by adding inert diluents, for instance) over a wide range. This becomes important in cases where the controlling regimes change as a function of time. For example, for a relatively nonporous solid in the initial time the reaction may be kinetically controlled when the observed order will correspond to the true order. At latter stages of reaction diffusional factors can become important due to formation of the product layer. Here the reaction will approach first order behavior with respect to the gas. To completely characterize the conversion-time behavior of such a system, an accurate value of the order of reaction is necessary and this can only be obtained by carrying out the reaction over a wide range of bulk gas concentrations of the reactant. The order with respect to the solid is also important if the experimental data are to be fitted with the volume reaction models. This is, however, a quantity which cannot be easily obtained unlike the order with respect to the gas phase species and may only have to be obtained by curve-fitting the experimental data. Other models do not require a knowledge of the order with respect to solid and instead require information such as pore size distribution.

The intrinsic reaction rate and the kinetic constants can only be obtained from rate vs time data. Here again data at different particle sizes and different gas velocities are useful in obtaining realistic model parameters. Also, as most gas-solid reactions are accompanied by significant heat effects, care should be taken to maintain isothermal conditions as far as possible. Further, temperature measurements at various positions in the pellet are extremely useful in assigning the correct temperature to the observed reaction rate.

Electron probe micrographs are proving to be of importance in model discrimination and parameter estimation in gas-solid systems. This technique provides a detailed concentration profile of the solid B as a function of radial position for various extents of reaction. With this additional data it is possible to match the concentration profile of B in the pellet with model predictions in addition to matching x-t data. This coupled with independent measurement of the porosity and effective diffusivity provides a powerful technique in model discrimination and parameter evaluation for gas-solid systems. Prasannan and Doraiswamy (1982) have discussed this technique in detail and applied it to obtain sulfur profiles in a pellet of zinc sulfide subjected to varying degrees of oxidation. Gibson and Harrison (1980) and Hartman and Coughlin (1976) have also used this technique in earlier studies.

Having obtained the data in the above manner, one can then proceed to model verification and parameter estimation. Here the choice of the model is often important. The most widely used model has been the sharp interface model due to its mathematical simplicity and this can fit the data easily over a limited range of operating parameters. However the model may not be satisfactory when extrapolated over a wide range of operating parameter values, especially for relatively porous pellets. Also, the model does not provide an insight into the phenomena involved in these processes. The volume reaction models are suitable for porous pellets but these models account for the structural changes that occur in the pellet in a purely empirical way. Such changes are important whenever the molal density of the product is different from that of the solid. The particle-pellet models are suitable when the solid is formed by compacting grains of fine size. In addition they are capable of accounting for the structural changes due to reaction and sintering in a rational manner. When the grains have no real physical meaning (that is, when the pellet is not formed by compaction) an appropriate grain size and shape will have to be ascribed in the model; thus empiricism is introduced to a certain extent. The single pore models have mathematical simplicity and very few adjustable parameters but have the disadvantage of inherent assumption of uniform pore size. Finally the distributed pore size model and the random pore model incorporate the structural characteristics in greater detail and hence are useful in fitting data for pellets of differing pore structures. Among the various distributed pore size models, the random pore model is mathematically simple and convenient to use as it does not require solution of detailed population balance equations.

A detailed experimental evaluation of the various models is likely to be extremely useful and this will require measurement of various properties of the solid as discussed earlier. Finally a comparison of various models with a set of complete and well characterized experimental data will be very useful in pointing out future directions of research in the mathematical modeling of these systems.

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NOTATION

a = dimensionless concentration of A at a position y in the pellet, A/A_g
A = species A or concentration of A at position y
A_1, A_2 = gaseous reactant species
A_{f_p} = rate constant for sintering (Eq. 44)
A_g = concentration of A in the bulk gas
b = dimensionless concentration of B at a position y in the pellet
B = concentration of reactant B at position y
B_1, B_2 = reactants present in the solid (Table 4)
B_o = concentrations of B in the pellet at time zero
Bi_H = Biot number for heat transfer, hR/D_e
Bi_M = Biot number for mass transfer, $k_g R/D_e$
Bi_p = Biot number for reaction in a particle, $D_{eG}/(k_s r_{Go})$
c_p = specific heat of solid pellet
C_m = cumulative concentration defined by Eq. 11

D_e = effective diffusivity of A in the pores of the solid B
D_{eo} = effective diffusivity at time zero
D_{eG} = effective diffusivity of gas A in the product layer
D_K = Knudsen diffusion coefficient for gas A
D_M = molecular diffusion coefficient
E = activation energy of reaction
E_s = activation energy for sintering
f_p = fraction of pores removed by sintering
$f(s)$ = pore number distribution in the pellet
$F(C_m)$ = functional dependency of rate on cumulative concentration
$F(f_p)$ = relative tortuosity factor due to sintering
$g(s)$ = pore length distribution function
G = product solid formed in the reaction
h = heat transfer coefficient in the external film
k_e = effective thermal conductivity of the pellet
k_g = gas film mass transfer coefficient
k_s = surface reaction rate constant
k_v = volume reaction rate constant
L_o = total length of the pores per unit volume of the pellet
m = order of reaction with respect to gas
M_B, M_G = molecular weight of species B and G respectively
n = order of reaction with respect to solid
N_0, N_1 = structural parameters in the capillary pore model
N_2, N_3 = transient heat accumulation parameters in the volume reaction and particle-pellet models respectively
$p(s)$ = probability density function in the capillary pore model
P = product gas species
r = radial distance in the pellet
r^* = dimensionless position of the reaction interface in a grain, r_{Gi}/r_{Go}
r_A = rate of reaction of A per unit pellet volume
r_G = radius of the grain at time t at position r
r_{Gi} = position of reaction interface within a grain
r_{Go} = initial grain radius
R = pellet radius
R_g = universal gas constant
s = pore radius
s_1, s_2 = dimensions of the single pore and the product layer formed around it
S_g = surface area of pellet per unit mass
S = reactive surface area of pellet at any given time (per unit volume of pellet)
S_F = shape factor of the pellet
S_o = reactive surface area at time zero
t = time elapsed
T = temperature of the pellet at position r
T_o = initial temperature of the pellet
T_M = Tamman temperature of the solid
v = reaction velocity defined as ds/dt
V = volume enclosed by reaction surface (per unit pellet volume) at time t
V_o = initial volume enclosed by reaction surface
x = conversion of the solid reactant B
y = dimensionless position in the pellet, r/R
z_v = ratio of molal volume of the product to the reactant

Greek Letters

β = thermicity parameter (Table 1)
γ = Arrhenius number (Table 1)
$(-\Delta H)$ = heat of reaction
ϵ = pellet porosity
ϵ_G = porosity of the product layer
ϵ_O = initial porosity of the pellet
θ = dimensionless temperature at position r, T/T_o
Ω, Ω_1 = dimensionless local rate of reaction in the volume reaction and particle-pellet models respectively
ϕ = Thiele modulus for volume reaction model
ϕ_1 = Thiele modulus for particle-pellet model
τ = dimensionless time for the volume reaction model
τ_1 = dimensionless time in the particle-pellet model
τ_2 = dimensionless time for the random pore model
τ_f = tortuosity factor of the pellet
ρ_B, ρ_G = density of solid B and G respectively
ρ_P = bulk density of solid
λ = position of the zone of completely reacted solid
Ψ = structural parameter in the random pore model
ν = stoichiometric coefficient for the species indicated in the subscript

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Shear History Effects in the Spinning of Polymers

During their industrial processing, polymer liquids are usually subjected to complex flow histories. In principle, these can be taken into account in the constitutive equations. In reality, difficulties arise for complex flows. This fact can be illustrated by the spinning process. Here, experiments are presented in which the upstream section of a spinning device has been changed systematically. A constitutive model and a calculation procedure are suggested that permit an analysis of the upstream effects in the spinning flow. The results indicate that this analysis predicts well the spinning dynamics in the present experiments, using shear flow characteristics for the liquids. It is also concluded that the spinning flow can be altered by upstream changes. The changes in structure seem to be the most pronounced ones.

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SCOPE

The fluid mechanics of polymer processing constitutes an industrial problem that has not been completely solved. Elongational flows, in particular transient ones as in spinning, turn out to be difficult to describe (Denn, 1980). Attempts to model spinning dynamics with rheological characteristics derived from shear flow data, have show systematic errors (Spearot and Metzner, 1972; Bankar et al., 1977; Chang and Denn, 1979). Some promising results using relaxation time distributions should, however, be mentioned (Phan-Thien, 1978).

An additional problem arises in the case of spinning. This type of flow is always preceeded by an upstream flow in a tube and a nozzle. The resulting initial conditions for the spinning line are normally incorporated in a rather arbitrary manner. Experimentally some shear history effects have been found by Oliver and Ashton (1976), but no quantitative interpretation was given.

Considering the more general interest of shear history effects in complex processing flows, some systematic experiments were performed. They include spinning flow with a variable shear history. As rheological constitutive equation, a structural kinetics model is used (De Cleyn and Mewis 1981) derived from that by Acierno et al. (1976). Model predictions of the spinning dynamics are used to assess the rheological model and to investigate the effect of shear history.

CONCLUSIONS AND SIGNIFICANCE

The suggested rheological model makes it possible to take into account relatively complex shear histories in spinning experiments. If the shear rate is not constant throughout the cross section, as in pipe flow, averaging over the structure distribution gives better results than averaging over the shear rate. The stress levels at the nozzle can be estimated directly as long as they are not affected by the spinning column. Experimentally some effect of flow history on the spinning dynamics of the polymer solutions under investigation is detected. However, the global effect is reduced somewhat by a compensation in the spinning flow. The interference becomes more obvious if the resulting structures are calculated. The effect can be associated with structural changes of a suitable characteristic time scale.

The rheological model and the calculation procedure used here provide a means to analyze relatively complicated flow patterns and suggest a route to the rational analysis of polymer processing operations. The model can also be used in numerical simulations. Further elaboration will be necessary in order to handle the even more complex situations of industrial processes.

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